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ANNUAL REPORT
on
Essential Oils, Synthetic Perfumes, &c.
Published by
SCHIMMEL & Co
MILTITZ
near Leipzig

EDITION 1921.

Sole Agents in the United States and Canada
FRITZSCHE BROTHERS, Inc.
82-84 BEEKMAN STREET, NEW YORK CITY.

Rosemary-Gathering on the Island of Lesina (Dalmatia).

(After a water-colour painting in the possession of the Perfumery Department of the German Museum in Munich. Gift of the firm of Schimmel & Co.)

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Contents.

Commercial Notes and Scientific Information on Essential Oils 5
Chemical Preparations and Drugs 52

Notes on Scientific Research Work in the Domain of Terpenes and Essential Oils.

- General 74
- Bibliography 87
- Analytical 88
- Physical 89
- Botanical 92
    - Phyto-physiological 94
- Pharmaco-physiological 95
- Chemical 97
    - Hydrocarbons 98
    - Alcohols 104
    - Aldehydes 106
    - Ketones 107
    - Phenols and Phenol Ethers 112
    - Acids, Esters and Lectones 113
    - Glucosides 117
    - Nitrogenous Bodies 118

List of abbreviations.

d = specific gravity.
d_{20° = specific gravity at 20° (in references from our laboratories uniformly compared with water at 15°).
$d^{20^\circ}_{4^\circ}$ = specific gravity at 20°, compared with water at 4°.
α_{D20° = optical rotation at 20°, in a 100 mm. tube.
$[\alpha]_D$ = specific rotation.
n_{D20° = index of refraction at 20°.
sol. p. = solidifying point.
m. p. = melting point.
b. p. = boiling point.
n = normal.
acet. = acetylation.
acid. v. = acid value; ester v. = ester value; sap. v. = saponification value.
g. = gram; cc. = cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.
The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

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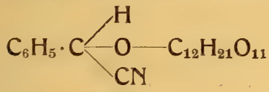
Commercial Notes and Scientific Information on Essential Oils.

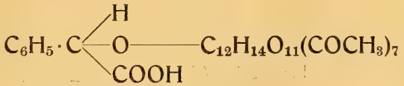
Almond Oil, bitter.—The formula (I) of a mandelo-nitrileglucoside, which is now accepted for the constitution of amygdalin, may be considered as well established. Attempts made to separate the disaccharide as such from the mandelic acid nitrile residue had in general merely led to the splitting of the glucoside into glucose and mandelic acid nitrile glucoside. Only recently Giaja[1] succeeded, by means of enzymes from the intestines of snails, in decomposing amygdalin directly into mandelic acid nitrile and a disaccharide. Little is known concerning the nature of this disaccharide which is supposed to be of the trehalose type and which does not reduce Fehling's solution. The assumption of E. Fischer, that this sugar was maltose or a very similar disaccharide, is not confirmed by the observations of Caldwell and Courtauld[2], H. ter Meulen[3] and A. Bau[4].

P. Karrer, C. Nägeli and L. Lang[5] have recently attempted to decide whether the amygdalin-disaccharide might possibly be cellobiose; they have been able to disprove this assumption. Not succeeding in the originally-intended synthesis of mandelo-nitrile-celloside, they prepared on the one hand, hepta-acetyl cellosido-mandelic acid (II, in crystals of m. p. 179 to 182°; $[\alpha]_D - 44°$) from inactive silver mandelate and aceto-bromocellobiose, and on the other hand from amygdalin, hepta-acetyl amygdalinic acid (amorphous, m. p. uncertain between 60 and 100°; $[\alpha]_D + 21°$). Since these two bodies, which were both hydrolysed by emulsin and were hence of glucoside character, were totally different from one another, it followed, that amygdalinic acid is not identical with cellosido-mandelic acid, and that the sugar of amygdalin cannot be a cellobiose.



$$C_6H_5\cdot C\begin{matrix}\diagup H\\ -O-C_{12}H_{21}O_{11}\\ \diagdown CN\end{matrix}$$

(I) Amygdalin.



$$C_6H_5\cdot C\begin{matrix}\diagup H\\ -O-C_{12}H_{14}O_{11}(COCH_3)_7\\ \diagdown COOH\end{matrix}$$

(II) Heptacetyl-cellosido-mandelic acid.

As regards Spanish bitter almond oils, see page 78 of this *Report.*

Alpine Rose Oil.—From young, air-dried shoots (125 g.) of the alpine rose, *Rhododendron ferrugineum,* L., which came from the Italian Alps (*La Madone des Fenêtres),* Roure-Bertrand Fils[6] prepared by extraction with petrolether and subsequent distillation 0.22 g. = 0.17 per cent. of essential oil; the light-green product of aromatic scent had the following properties:— $d_{15°}$ 0.840, almost insoluble in alcohol of 90 per cent.; acid v. 0, sap. v. 63.47[7].

---

[1] *Compt. rend.* **150** (1910), 793. — [2] *Journ. chem. Soc.* **91** (1907), 666, 671. — [3] *Recueil trav. chim. des P.-B.* **24** (1905), 461. — [4] Cf. *Report* **1917**, 3. — [5] *Helvet. chim. acta* **3** (1920), 573. — [6] *Bull. Roure-Bertrand Fils,* April **1920**, 34. — [7] Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. III, p. 384.

Angelica Oil.—There is an almost unprecedented scarcity of this oil. The small quantities of angelica root which Thuringia supplied last autumn were too expensive for profitable oil extraction. After clearing our stock of last year we are hence no longer in a position to offer angelica oil. We must hope with our clients for better new crops. Our own cultivations will become productive again this year. We shall thus at least be in a position to cover the most urgent demands. The dry spring has, however, not exactly been favourable to the development of these plants.

Apple Oil.—As regards the chemical nature of the substances, upon which the characteristic odour of ripe fruit depends, little was known so far. C. Kleber1) showed that ripe bananas contained amylacetate besides traces of a phenol body; and C. Thomae2) made several communications concerning the products of distillation of fresh apple-parings without, however, giving any detailed information concerning the quantities and the nature of the substances obtained.

The comprehensive studies of F. B. Power and V. K. Chesnut3) concerning the odoriferous constituents of apples will all the more more be interesting. In general it may be said that the bodies, to which the aroma of fruits is ascribed, have been considered to be esters, simply for the reason that various artificial compounds of this type recalled in their scent certain fruit. Thus amyl valerate is known in the trade as apple oil, amyl acetate as pear oil, and ethyl butyrate as pineapple oil, although so far it has not been established with any degree of certainty what chemical compositions the genuine apple oil, pear oil and pineapple oil may really possess.

The authors made use of three different sorts of apples (Ben Davis, crab and Springdale) which were all taken from the experimental station at Arlington, Va. The fruits were highly fragrant after having been stored for some time in a cellar. They were carefully pared by means of a machine in such a way that only a thin skin of the inner white fruit adhered to the paring. From 805 kg. of Ben Davis apples they obtained about 161 kg. of parings which were at once submitted to steam distillation, without any addition of water. Altogether 163 litres of a somewhat opalescent distillate were collected which clarified in a few days and deposited some solid substance on the sides of the vessel. The liquid possessed the sweet fragrance characteristic of fresh, ripe apples to a high degree. The first portions of the distillate were neutral.

When the aqueous liquid had been poured off, the just-mentioned solid constituents were dissolved in ether. The authors thus obtained 0.04 g. of a colourless substance which, dried on a porous plate, yielded thin, satiny laminæ of a melting point of 63 degrees. The substance probably represented triacontane, $C_{20}H_{62}$, not quite pure. From the main portion of the distillate they further prepared by repeated distillation in a current of steam one litre of a liquid in which the following compounds were found:— Furfural (light-red coloration with aniline and hydrochloric acid); acetaldehyde (in solutions of dimethylamine (of 33 per cent.) and sodium nitroprusside (of 1 per cent.), a beautiful indigo-blue colour was produced which soon turned into brown or yellow); amylalcohol (about 0.00065 per cent., calculated upon the weight of the apples; oxidation to valeric acid and analysis of the silver salt of the acid); traces of methylalcohol (oxidation to formaldehyde by the process of Denigès and von Fellenberg)4); further, formic, acetic, caproic and caprylic acids (analyses of the silver salts).

---

1) Cf. *Report* April 1913, 29. — 2) *Ibidem* 28. — 3) *Journ. Americ. chem. Soc.* 42 (1920), 1509. — 4) *Biochem. Zeitschr.* 85 (1918), 45.

From 57 litres of the distillate (corresponding to 54 kg. of parings) they obtained 1.905 g. of an essential oil representing 0.0035 per cent. of the parings (0.0007 per cent. of the whole fruit) in the following way:— The distillate was repeatedly submitted to distillation in a current of steam until the volatile products had been concentrated in 8 litres of water. The oil was extracted from this liquid by means of ether. The oil obtained was a yellow, somewhat viscous liquid which turned darker in the course of time and smelt of fresh apples. Cooled a little below the ordinary temperature the liquid changed into a soft mass. Some very tiny needle-shaped crystals segregated; they were probably identical with the already-mentioned triacontane. Shaken with a little water a few drops of the oil gave the acetaldehyde and furfural reactions. The oil further contained the amyl esters of formic, acetic and caproic acids and a very small quantity of the ester of caprylic acid.

In the aqueous distillate from the Springdale apples the presence of small quantities of methyl alcohol (according to von Fellenberg)[1]) and of ethylalcohol (iodoform reaction) could distinctly be established in addition to the already-mentioned compounds. It could not be decided, however, whether the methyl alcohol was present as such in the parings or perhaps as methyl ester of the pectin acid[2]).

The examination of the parings of the crab apples led to similar results. The proportion of essential oil was somewhat higher and amounted to 0.0043 per cent. of the parings, or to about 0.0013 per cent. of the whole fruit.

Whilst in the first-studied species of apples the presence of acetaldehyde could only be established by means of the reaction with dimethylamine and sodium nitroprusside, the authors were able to determine the aldehyde in the distillate of the crab apples quantitatively as silver acetate by precipitating it by means of sodium bisulphite and oxidising it to acetic acid. At the same time it was demonstrated that formaldehyde was absent, and that only traces of an apparently higher homologue were present. The proportion of acetaldehyde amounted to about 0.001 per cent. of the apple parings.

So far it had been assumed that the lower aliphatic aldehydes were not present as such in the plant, but were only formed during the distillation. Since now the authors had in this case actually found relatively large proportions of acetaldehyde, they further attempted to determine whether this aldehyde was present already in the odoriferous constituents of the apples, or whether it was produced at a later stage.

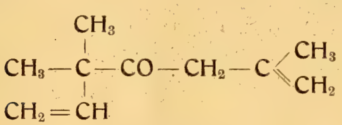
For this purpose 215 sound, red Nero apples (35.85 kilos) were put in a copper boiler, provided with a tightly-fitting cover and with two small openings, above and below. A current of air was drawn through the boiler, and this air had first been purified with alkaline potassium permanganate solution and concentrated sulphuric acid and had finally been passed through about 300 cc. of a saturated solution of sodium bisulphite. The experiment lasted 7 or 8 days. At the end of this period the bisulphite had bound a sufficient amount of acetaldehyde for definitely proving its presence by means of ammoniacal solution of silver oxide, Schiff's reagent, and of dimethylamine and sodium nitroprusside. Acetaldehyde is, therefore, a product of the living cell of the fruit and is present as such in the odoriferous compounds of ripe apples. The establishment of this fact is of importance for biologists. The growth of the scald, which affects some apples when stored without sufficient circulation of air and which is caused by a fungus (*Fusicladium pyrinum*, Fuckel), may favourably be influenced, for instance by the presence of acetaldehyde.

---

[1]) *loc. cit.* — [2]) Cf. Tschirch, *Arch. der Pharm.* 252 (1914), 538.

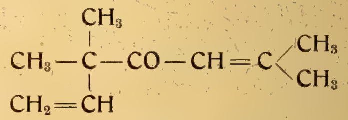
We should finally emphasise that amylvalerate, the so-called apple oil, is not a constituent of the apple paring. The characteristic odour is exclusively due to the compounds which have been identified in this research. Small differences in the aroma are to be ascribed to different proportions of these compounds.

Oil of Artemisia annua. — In a second research on the artemisia-ketone Y. Asahina and S. Takagi[1]) state that the body $C_{10}H_{16}O$, which they had previously[2]) isolated from *Artemisia annua,* L. and which they had called artemisia ketone, further contains an isomeride, an *iso*-artemisia ketone. From the mother liquor of the artemisia ketone-semicarbazone they were able to isolate the semicarbazone of this new *iso*-ketone (m. p. of the hydrated compound 70 to 72°, of the anhydrous 103° to 104°). The free *iso*-artemisia ketone; b. p. 182 to 183°; $d_{4^\circ}^{17^\circ}$ 0.8711; $[\alpha]_D \pm 0$; n_{D17° 1.4688; mol. refr. 47.425 (calculated for $C_{10}H_{26}O/\overline{_2}$ 47.45); resembled in its physical properties the artemisia ketone; the catalytical reduction yielded a tetrahydro-derivative, which was identical with the tetrahydro-artemisia ketone. Oxidised with dichromate and sulphuric acid the latter gave dimethylmalonic acid, in addition to acetone (?)[3]) and acetic acid. The artemisia ketone itself yielded with potassium permanganate considerable amounts of dimethyl-malonic acid. Heated with alcoholic sulphuric acid the ketone passed quantitatively into the *iso*-compound. The authors, therefore, conclude that the two isomerides differ only with respect to the position of the double bond and that the compounds have the following constitutional formulæ: —



$$CH_3-\underset{\underset{CH_2=CH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CO-CH_2-C\begin{smallmatrix}\diagup CH_3\\ \diagdown CH_2\end{smallmatrix}$$

Artemisia ketone.



$$CH_3-\underset{\underset{CH_2=CH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CO-CH=C\begin{smallmatrix}\diagup CH_3\\ \diagdown CH_3\end{smallmatrix}$$

Iso-artemisia ketone.

Oil of Artemisia glutinosa. — C. T. Bennett[4]) reports on an essential oil of a species of artemisia, which was not known so far and which grows in Murcia, Spain, *Artemisia glutinosa,* Gay. The oil has a pleasant aromatic odour which recalls a mixture of the oils of sage, rosemary, and spikenard and which has the following constants: — d 0.937; $\alpha_D + 24^\circ$; n_{D20° 1.4780; soluble in 1 to 2 vol. of alcohol of 80 per cent. (turns turbid with more alcohol); ester (calculated as bornylacetate) 6.3 per cent.; total alcohol (calculated as borneol) 17.5 per cent.; phenols 8 per cent.; aldehydes and ketones 18 per cent.

Of this oil, which began to boil at 175°, 52 per cent. distilled below 200°. It consisted to a large degree of terpenes, probably of terpinene or dipentene; pinene was not present; the phenols (methylchavicol?) gave with iron chloride a violet coloration. Thujone was not found, but a small quantity of a pleasant-scented aldehyde was isolated. Bennett mentions that this only species of artemisia of Spanish origin so far known to yield an essential oil, which consists almost completely of thujone, was *Artemisia Barrelieri,* Bess. It should be pointed out, however, that Bernabé Dorronsoro has recently also investigated the essential oil of wormwood plant cultivated in Malaga[5]) and has found in this 57.50 per cent. of thujone (cf. page 83 of this *Report*).

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[1]) *Yakugakuzasshi (Journ. pharm. Soc. of Japan)* No. 464. **1920,** 873. Reprint was kindly sent to us. — [2]) Cf. *Report* **1918,** 8. — [3]) The note of interrogation is taken over from the original paper. — [4]) *Perf. Record* **11** (1920), 286. — [5]) The plant source is not further specified.

Bay Oil.—In our last *Report* (page 7) we mentioned that the cultivation of the bay tree was making great progress in the West Indies. The yield of oil has constantly been increasing, and the average phenol content of the product has, in the year 1917, risen from 50 to 55 per cent. Nevertheless, we see from English notices[1]), the growers and distillers of the West Indies were hesitating to extend the bay oil industry any further, lest the production should exceed the demand. An over-production would only have to be apprehended, however, if the bay oil should fetch higher prices than the cassia, thyme, and lemongrass oils. If the general condition of the market in essential oils were taken into consideration, a better demand for bay oil should soon be expected.

The total exports of bay rum from the Virgin Islands amounted in the year 1919 to 84545 gallons of value 66789 $[2]). Of this 9012 gallons went to the United States of America. These figures are considerably higher than those for the year 1918 which, owing to transport difficulties and other consequences of the war, remained below normal. For the year 1920 a further rise in the value of the exports may be predicted, though the quantity may remain below that of 1919. Within the first 6 months of 1920, 33852 gallons of a value of 36026 dollars were exported.

The bay oil industry is not yet sufficiently organised and is consequently exploited to an incomplete degree.

Birch Bud Oil has once more become available in fairly-sufficient quantities, a fact which we should point out in this place. This news will be welcomed by the numerous manufacturers of birch hair washes &c., for this product, and especially our most readily-soluble quality, has sadly been missed for a long time. The procuration of this material involved considerable difficulties and expenses which could not but affect the prices.

Oil of Sweet Birch.—As regards the characteristic reactions of this oil, see page 48 of this *Report*.

As regards the determination of birchbark oil, wintergreen oil and synthetic methyl salicylate, see page 48 of this *Report*.

Oil of Brassica campestris chinoleifera (Colza Seed Mustard Oil).—The imports of European rape seed and mustard seed into America having almost completely ceased of late, Chinese and Japanese substitution products have found their way again into the States in their place. Thus Chinese colza was offered as a substitute for mustard seed and it was bought, although neither the taste, nor its physiological properties fitted it for the purpose. The Chinese colza seeds come, according to A. Viehoever[3]) from the crucifere *Brassica campestris chinoleifera n. sp.* Viehoever, which grows in China. They are a little smaller than white mustard seed which they strongly resemble. They contain 0.4 to 0.6 per cent. of crotonyl mustard oil[4]) in the form of a glucoside. According to Viehoever this oil is not poisonous, in contradistinction from the allyl mustard oil present in the black mustard seed. For this reason, it is said, the Chinese colza seed cake is a more harmless fodder than the Indian colza seed cake which frequently contains mustard seed.

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[1]) *Perf. Record* **11** (1920), 121. — [2]) *Ibid.* 332. — [3]) *Journ. Americ. pharm. Assoc.* **10** (1921), 16. — [4]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 527.

Buchu Leaf Oil.—The imports from South Africa of buchu leaves[1]) were

	weight	value
1917	124 110 lb.	20 154 £
1918	89 675 „	16 948 „

The countries of import were Great Britain and, above all, the United States of America, since the main portion of the drug coming to England went further to America. As we mentioned already, a few years[2]) ago, the gathering and the sale of buchu leaves is under legislative control in the Cape Colony. The Government[3]) has recently made this control more stringent, and it is not surprising that the export of buchu leaves is constantly decreasing.

In the last few years attempts have been made to cultivate the buchu shrub in Kirstenbosch, in the National Botanic Gardens. On the sunny hillsides of the Wynberg, where the soil consistes of a red sandy loam, rich in iron and poor in lime, the seeds of *Barosma betulina* which had been planted in 1914, were doing well. In June 1916 further seeds were, in the same spot, put in rows 4 feet apart, the soil not having been manured. Of these seeds 80 per cent. developed, though slowly. Of the seeds raised in tins, which had been kept moist, only 20 per cent. germinated. The experiments indicated that the seeds do not bear moisture well during germination. The replanting of the seedlings when about one year old was also connected with great losses (50 per cent.).

To gather the leaves, the plant, when about eighteen months old, is cut back to nearly the crown in the first instance, cutting in each successive season a little above the previous year. In this way it is possible to gather every year and to realise gradually increasing crops.

In May 1918 shrubs two years old, standing in a row 80 yards long, gave $8^1/_2$ lbs. of dry leaves. With a distance between the rows of about 4 feet this quantity would correspond to a yield of 400 lbs. per acre. After harvesting the cut down plants throve quite satisfactorily; none of them died.

The experiments made in Kirstenbosch have, therefore, shown that the cultivation of the buchu shrub will be profitable under certain conditions; but the cultivation should be limited to the *Barosma betulina*, Bartl., which is the favourite species. This plant thrives especially on dry, sunny hillsides where other kinds do not prosper.

Camphor Oil.—We mentioned in our last *Report,* on page 12, that P. Carmody had estimated the annual demand of the world for camphor at 10 million pounds. According to other information[4]) the demand for camphor had, already before the war, been estimated at 12 and even 16 million pounds per year. The latter figures are probably the more correct, particularly in view of the fact that the demand for camphor has increased considerably during the last 20 years and that it far exceeds the supply. The deficiency of camphor made itself particularly felt during the war, when the synthetic camphor which was made principally in Germany disappeared from the market. In spite of the strong demand the camphor production went steadily down, even in the chief country of its production, Japan. By the end of 1918 the Japanese Government had appointed a commission to enquire into the causes of this diminution. The results of this enquiry have not yet become publicly known. The Government further sent several expeditions under military escort into the interior of Formosa in order

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[1]) *Bull. Imp. Inst.* **17** (1919), 588. — [2]) Cf. *Report* **1918**, 10. — [3]) *Chemist and Druggist* **92** (1920), 909 — [4]) *Weltwirtsch. Nachr., Inst. f. Weltwirtsch. u. Seeverkehr in Kiel* **1921**, No. 284, p. 2215.

to explore the camphor forests. It is hoped that in at least three years the gathering of camphor will be resumed also in that country.

Since 1916 the Japanese Government, which has made the camphor production in Japan a monopoly, has been striving to work the total crops up in the country itself and to permit only the export of refined camphor. The administration of this monopoly has decided to supply to foreign refineries, instead of crude camphor, only certain definite quantities of refined camphor through the Nippon Camphor Refining Company at prices which are 10 per cent. below the market price. The following figures will show, that this restriction does not appear to have been enforced in all cases. In the year 1919, 1.42 million pounds of crude camphor (by comparison with 2.5 million pounds before the war) are still said to have been exported to America[1]. In the first three months of 1920, 100 000 kin were assigned to Great Britain and 42 000 kin to France, in both cases of BB-camphor, whilst only 25 000 kin of crude B-camphor were sent to America[2].

Since in spite of the diminishing exports the needs of the Japanese industry could no longer be satisfied within the last two years, the allowance of camphor to celluloid factories was also rationed. Several firms which, during the war had been engaged in the production of war material and which had extended their establishments, were in consequence obliged to limit their production considerably. Of the camphor refineries, which were founded in the years 1917 and 1918, the Formosa Camphor Refining Company was said to consume 1½ million pounds, and the Nippon Camphor Refining Co. even 6½ million pounds of camphor, per year.

According to a paragraph in the *Industrie- und Handelszeitung*[3] the camphor production in Japan has, thanks to the measures taken by the Japanese Camphor Office, risen in the year 1919 to nearly 6.7 million pounds. Of these Formosa supplied about 5.7 million. In the year previous only half as much camphor had been produced.

As regards the camphor production of China we gave some figures in last year's *Report*, on page 11. According to the *Yakugyo-Shuho*[4], 350 000 kin of camphor were produced in 1919 in the province of Kiangsi, and further 300 000 kin of camphor oil. For 1920 a yield of only 250 000 kin of camphor oil was reckoned upon. Most of this camphor goes to the factories in Shanghai.

The English journal, from which we quote, also brings some statements, the critique of which we leave to our readers. Thus it is said that the distillate of the leaves of the camphor tree had been contaminated with large portions of resin and chlorophyll. Further — in speaking of the synthetic preparation of camphor from oil of turpentine — "it is much to be regretted that they cut down the trees in France[5] in order to gain the turpentine". Finally the remark is not missing that the Germans were responsible even for this deficiency of camphor from which the world is now suffering.

The stocks of camphor and of camphor oil in Foochow, which were in June 1920 in the hands of the traders, were estimated at 80 000 and 40 000 lbs., whilst the Government Camphor Office had stored some 27 000 lbs. of camphor. Owing to the want of enquiries from Hongkong and to the difficulties of manufacture and of transport, the camphor price fell from 200 tael to 98 tael per picul (1 picul = 60.453 kg.),

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[1] *Ind. u. Handelsztg.* No. 35 of 11. II. 1921, supplement. — [2] *Ibid.* No. 252 of 5. XI. 1920, supplement. — [3] *Ibid.* No. 35 of 11. II. 1921, supplement. — [4] *Chemist and Druggist* 93 (1920), 1310. — [5] In France turpentine is obtained by a special tapping process (*Gemmage à vie* and *Gemmage à mort*). Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 72.

and for oil to 40 tael per picul. From 1919 up till March 1920 the exports from Foochow were considerably larger than those of 1918[1].

The most important camphor districts are Kienning, Yuchi, Yungan, Yenping, Tatien, Shaowu, Shasien and Ningte. There camphor and its oil are manufactured by means of very simple distillation appliances on the spot, as E. B. Price[2] reports. The camphor which is crystallising is collected and sold at first quality. The liquid constituents have once more to be distilled. This second distillation, which takes place in Foochow, yields from 133 pounds of camphor oil, 64 pounds of camphor and 27 pounds of oil, the latter serving as basis for inks and colouring materials. The camphor which is gained from the oil is less good than the product of the first distillation.

There are in Foochow 12 camphor oil factories of which 9 belong to the Chinese, 2 to the Japanese and one to the Portuguese. The daily production of each factory averages 325 lbs. of camphor. The campher industry is rather highly taxed; private undertakers, moreover, have to obtain official permission before they can erect any new works. The Japanese distillers of Foochow are exempt from this tax.

According to the *Pekin Daily News*[3] the Japanese Government has purchased the monopoly of the exploitation of camphor in this province from the governor of Fukien. In Kiangsi, Japan is attempting to proceed on similar lines. The native population of the capital of the province are making united efforts to stop this procedure of the Japanese.

Camphor Exports from Foochow.—The main bulk of the camphor, which is produced in the Chinese province of Fukien and which is estimated at about 800000 kin annually, is exported via Foochow. These exports from Foochow amounted in the year 1907 to 394 picul, in 1918 to 424 picul, in 1919 to 6987 picul, and in the first half of 1920 to 5000 picul. The consumption of camphor in Europe and America amounted in the year 1918 to 2160000 kin and in Japan 2600000 kin, a total of 4760000 kin. Of these only 600000 kin were, however, of Chinese origin. The price which, by the end of 1919, had been 170 tael per picul, fell by March 1920 to 130 tael and declined further down to 100 tael[4].

A paper by J. L. Simonsen and T. P. Ghose[5] gives information concerning the contents of camphor and of camphor oil in camphor trees of different ages which had grown in the plantations of Dehra Dun, Burma, Madras, Cochinchina, and Calcutta. Since it was known from former investigations[6], to which degree the ratio between solid camphor and camphor oil fluctuates with the age of the tree and with the season, and how large quantities of oil will be found in the different parts of trees of different ages, we shall content ourselves in this place with summarising the tabular statements made in this paper.

The leaves of coppice camphor trees of Dehra Dun had in different seasons of the years 1917 to 1919 a content of camphor ranging from 0.25 to 0.84 per cent. and of camphor oil ranging from 1.63 to 4.24 per cent. Small twigs cut from the same trees contained from 0.19 to 0.61 per cent. of camphor oil, and parts of the trunk of trees, from 17 to 22 years of age, contained from 0.97 and 0.69 per cent. of camphor and from 0.86 and 0.69 per cent. respectively of camphor oil.

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[1] *Ind. u. Handelsztg.* No. 234 of 16. X. 1920, supplement. *Chem. and met. Eng.* **23** (1920), 844. — [2] *Americ. Journ. Pharm.* **92** (1920), 923. After *Commerce Reports* of 18. VIII. 1920. — [3] *Ind. u. Handelsztg.* No. 46 of 24. II. 1921, supplement. — [4] *The Yakugyo-Shuho*, Tokyo of 8. VIII. 1920, p. 4. — [5] *Journ. Soc. chem. Ind.* **39** (1920), 296. — [6] Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 465; *Report* 1918, 13.

The pale-yellow camphor leaf oil had the following constants: — $d_{30^\circ}^{30^\circ}$ 0.9165; α_{D30° + 32.740°; n_{D30° 1.47; camphor 38 per cent. The distillation (705 mm.) gave the following fractions: — 150 to 190°, 41.7 per cent. ($d_{30^\circ}^{30^\circ}$ 0.8795; $[\alpha]$ + 25.55°; n_D 1,463); 190 to 212°, 39 per cent. (semisolid, containing 22.2 per cent. of camphor); above 212°, 19.3 per cent. The three fractions were further separated into 15 fractions (155 to 240° and above) in which the following bodies were identified: — *d*-*α*-pinene (nitrolpiperide, m. p. 118 to 119°); dipentene (tetrabromide (m. p. 125°); cineole (2.1 per cent., phosphoric acid method); terpineol; caryophyllene¹) (the nitrosate decomposed at 173°; caryophyllene alcohol, m. p. 95 to 96°); traces of cadinene (reaction with acetic anhydride and concentrated sulphuric acid); blue oil (b. p. 170 to 210° [40 mm]). Safrole, which was identified in the camphor wood oil, was not present.

The twig oil was dark brown and had the constants: — $d_{30^\circ}^{30^\circ}$ 0.8777; n_{D30° 1.473; it contained camphor, no cineole, and otherwise the same constituents as the leaf oil.

The pale-yellow camphor wood oil had the constants $d_{30^\circ}^{30^\circ}$ 0.9313; $[\alpha]$ + 34.44°; n_{D30° 1.4767; it contained safrole, caryophyllene and cadinene, but no cineole and no blue oil. In a fraction of high boiling point a terpene was isolated which was probably identical with camphoracene (? camphorene is possibly meant), the dipentene²) found by Semmler and Rosenberg.

The authors come to the conclusion that the distillation of the leaves cut from camphor trees may well repay itself. It should, however, further be investigated, how many times the leaves may be reaped, and what amount of camphor and camphor oil may then be expected.

Caraway Oil.—There are unfortunately no statistics available concerning the Dutch caraway market. It is said that there are still some 70 or 80000 bales from different harvests, partly of very doubtful quality, on sale in Holland, a large portion of which is in the hands of speculators. The last harvest yielded at the best 18000 bales, the greater portion of which has already gone abroad. There is a strong temptation to sell seed of 1920 mixed with old seed in order to get rid of the stocks of inferior old caraway, and it is probably owing to this reason that the samples of the last harvest submitted for examination have largely shown little-satisfactory oil contents. The prices for old seeds have dropped from 40 fl. per 50 kilos (war price) gradually down to 14 to 15 fl., whilst in 1920 seed fetched a better price, although large business has hardly been done. There is reason now to talk of a firmer tone in the market, because little caraway is said to have been cultivated last year and this spring, the peasants not feeling tempted by the prices. In view of the large stocks of which we have spoken the hopes of a rise in prices appear yet unjustified.

In Germany much caraway from East Frisia and Thuringia has gone to the distilleries, because the present valuta made the purchase of Dutch seeds difficult, and people were naturally inclined to give the German products preference.

The caraway plant, the roots and fruit of which are utilised by the Arabs as a spice, is cultivated in Morocco, particularly near Mekinez. In the year 1917 about 10 tons, corresponding to two-thirds of the harvest of caraway seeds, were exported³).

Champaca Oil. — With regard to champaca oil from the Philippines, see page 85 of this *Report.*

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¹) Caryophyllene has so far not been observed in camphor oils. — ²) Cf. *Report* October 1913, 34. — ³) *Rev. des produits chim.* **22** (1919), 647.

Chenopodium Oil, see Wormseed Oil, p. 49.

Chieh Oil.—See Sheih Oil, p. 43 of this *Report*.

Cinnamon Oil, Ceylon.—We take the following notes from an English paper[1] on the cinnamon industry of Ceylon which does not contain much novel information, but is supplementary to former statements on the subject[2].

Ceylon cinnamon is known to be superior in fine quality to all other kinds. This quality is due to the circumstance that the cinnamon tree finds just in Ceylon favourable conditions for its growth (a suitable temperature, in the mean 85° F = 29.5° C, and ample moisture). The trees attain in Ceylon a high age and not rarely a height of 40 ft. The shoots (as a rule 4 to 7) are cut every two years. They are dried by exposure to the air (sweating process) before the bark is peeled from the trunk. When the bark has turned soft after a while, the external layer of cork is peeled off. This portion, as well as the inner and thicker parts of the bark, are brought into the trade as a second-class article in the form of chips; the chips serve chiefly for the distillation of the essential oils[3]. In drying the pieces, about 3 ft. long, assume the shape of rolls or quills which are pushed into one another, and these "pipes" are shipped in bundles.

By far the largest portion of the cinnamon goes to the Romanic countries, Spain, Mexico, Central and South America, not so much to the United States of North America.

The cinnamon oil coming from Annam had, according to Roure-Bertrand Fils[4], the following constants:—d_{15° 1.051; α_D — 0° 8′; n_{D27° 1.6090; acid v. 2.8; soluble in 1 vol. and more of 70 per cent. alcohol; aldehyde contents 95 per cent. The oil, which had the amber yellow colour of cinnamon oil from Ceylon[5], had a sharper and less refined odour than this oil and a sharp burning taste.

As regards oils from *Cinnamomum Mercadoi*, Vid., and from *C. zeylanicum* from the Philippines, cf. page 85 of this *Report*.

Citronella Oil.—Within the last years the following weights of citronella oil have been exported from Ceylon *via* Colombo and Galle[6].

1917.	1918.	1919.	1920.
1211197 lbs.	1048202 lbs.	1045334 lbs.	1007412 lbs.

Of these went to the United States of America in 1919 377940 lbs., in 1920 480912 lbs.; to England in 1919 336701 lbs., in 1920 249963 lbs.; to France in 1918 4421 lbs., in 1919 140775 lbs., in 1920 54946 lbs.; to the Netherlands in 1919 31528 lbs., in 1920 9869 lbs.; to Italy in 1919 23321 lbs., in 1920 9076 lbs.; to Germany in 1920 8324 lbs. From Java and Madura[7] they exported in 1919 528534 kg., and in 1920 434245 kg. of citronella oil.

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[1] *Chem. and met. Eng.* **23** (1920), 684. — [2] Detailed information concerning the cinnamon tree, its cultivation and the treatment and utilisation of the bark will be found in Tschirch "*Ind. Heil- und Nutzpflanzen*". Berlin 1892, p. 86. — [3] Schimmel & Co. had introduced this process of preparing cinnamon oil in Germany in 1872; cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 418. — [4] *Bull. Roure-Bertrand Fils*, Oct. **1920**, N°. 2, 36. — [5] The properties make the oil comparable only to the Chinese, but not to the Ceylon distillate. — [6] *Perfum. Record* **12** (1921), 35. — [7] *Handelsberichten (Den Haag)* **15** (1921), 124.

Clove Oil.—The difficulties which the authorities place generally in the way of the imports of spices, the justification of which is a debatable question, having been overcome by measures which the industry took on its own account, this important oil is again being manufactured on a large scale. Clove stems are also being imported again in considerable quantities. Of the latter, large bulks have accummulated in Zanzibar and have for the present not found any satisfactory sale. The prices for cloves and clove stems have much been lowered of late, and the large stocks available in all the chief markets justify the expectation of further price reduction. We spoke in our last report of the rumoured erection of clove oil factories on the islands of Zanzibar and Pemba. So far there have been no confirmations of these news.

Coriander Oil.—The cultivation of coriander occupied in the year 1917 in Morocco an area of 2590 hectares, principally in the Shauya. In localities, where conditions were considered favourable and good results were obtained, an extension of the plantations is being contemplated. The cwt. of coriander was in 1919 paid 115 fr., against 25 fr. before the war[1].

Cumin Oil.—Among the aromatic plants of Morocco the Roman caraway, the cultivation of which covers an area of 5400 ha., claims the first place. The fruit are a favourite spice of the oriental nations. In Marrakesh the cwt of cumin cost in 1919 110 fr. The exports of cumin fruit amounted in 1916 to 1100 tons[2].

Oil from Cymbopogon javanensis.—The inaugural dissertation by J. J. Hofmann on the essential oil of a species of *Cymbopogon,* which we mentioned on page 20 of our *Report* of 1919, has been reproduced in the *Pharm. Weekblad* 56 (1919), 1279[3].

Cypress Oil.—As to Spanish Cypress Oil, see page 75 of this *Report.*

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[1] *Rev. des produits chim.* 22 (1919), 648. — [2] *Ibidem* p. 647. — [3] *Apotheker Ztg.* 43 (1920), 652.

Essential Oils, Sicilian and Calabrian.

The imports, for the year 1920, of essential oils shipped from Messina, the leading port, are summarised in the following table.

Statistics of Exports of Oils from Messina, 1920.

Country of Destination	Lemon oil Kg. net	Bergamot oil Kg. net	Orange oil Kg. net	Mandarin oil Kg. net	Other Agrumen oils Kg. net
Austria	619	—	73	—	—
Belgium	652	294	120	—	—
Czecho-Slovakia	595	120	200	10	—
Denmark	810	165	25	—	25
Egypt	500	—	—	—	—
France	26 318	27 954	5 745	10	310
Germany	7 223	2 977	3 167	—	—
Great Britain	125 537	27 326	8 137	1100	193
Greece	350	62	—	—	50
Japan	647	1 636	—	—	—
British India	329	94	14	—	24
Norway	560	—	104	—	—
Netherlands	2 867	1 025	700	25	—
Rumania	1 917	1 091	262	—	—
Spain	3 951	461	150	—	—
Sweden	942	180	65	—	35
Switzerland	737	400	—	—	—
Turkey in Europe	1 075	280	40	—	—
Australia	8 467	525	326	14	—
British South Africa	265	—	—	—	—
Argentina	3 687	1 338	205	—	—
Brazil	96	50	—	—	—
United States of America	246 761	15 510	30 723	921	—
Uruguay	422	150	—	—	—
Total kg. net	435 327	81 638	50 056	2080	637

Total . . . Kg. net 569 738 in 1920.
Against . . „ „ 611 237 „ 1919.

The export figures for the months of the years are:—

		1920.	1919.
January	kg. gross	66 865.—	42 710.—
February	„ „	173 851.—	28 618.—
March	„ „	105 497.—	75 335.—
April	„ „	108 987.—	52 406.—
May	„ „	70 009.—	151 913.—
June	„ „	85 988.—	109 814.—
July	„ „	48 397.—	72 731.—
August	„ „	27 310.—	107 184.—
September	„ „	49 214.—	36 720.—
October	„ „	51 198.—	157 957.—
November	„ „	44 691.—	81 338.—
December	„ „	72 868.—	102 002.—
	kg. gross	904 875.—¹)	1 018 728.—¹)

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¹) The net weight is obtained by deducting 40 per cent.

Average Prices of the Oils in the months October 1920 to March 1921.

Prices in Italian lire per Sicilian pound of 317 grams.

Year	Month	Lemon oil	Bergamot oil	Orange oil, sweet	Orange oil, bitter	Mandarin oil
1920	October: 2nd to 9th	14.50	95.—	65.—	46.50	97.50
„	„ 11th „ 16th	15.75	110.—	59.—	48.—	100.—
„	„ 18th „ 23rd	15.40	110.—	51.—	45.—	95.—
„	„ 25th „ 30th	15. –	108.—	47.—	43.—	98.—
„	November: 1st „ 6th	14.70	105.50	46.—	41.50	100.—
„	„ 8th „ 13th	14.25	100.—	45.—	41.—	110.—
„	„ 15th „ 20th	13.75	100.—	53.—	42.—	135.—
„	„ 22nd „ 30th	13.—	100.—	60.—	43.—	135.—
„	December: 1st „ 4th	13.—	97.—	55.—	42.—	120.—
„	„ 6th „ 11th	12.50	95.—	53.—	40.—	115.—
„	„ 13th „ 18th	12.—	92.—	50.—	38.—	110.—
„	„ 20th „ 31st	11.40	87.—	47.—	35.—	100.—
1921	January: 3rd „ 8th	11.75	82.—	46.—	35.—	100.—
„	„ 10th „ 15th	11.75	81.—	46.—	34.—	95.—
„	„ 17th „ 22nd	11.—	80.—	45.—	32.—	95.—
„	„ 24th „ 31st	10.—	79.—	44.—	31.—	93.—
„	February: 1st „ 5th	9.50	77.—	43.—	32.—	90.—
„	„ 7th „ 12th	9.50	77.—	43.—	32.—	85.—
„	„ 14th „ 19th	9.50	77.—	43.	32.—	85.—
„	„ 21st „ 26th	9.25	75.—	42.50	31.—	83.—
„	March: 1st „ 5th	8.50	73.—	41.—	30.—	80.—
„	„ 7th „ 12th	8.50	72.—	40.—	28.—	78.—
„	„ 14th „ 19th	8.50	70.—	40.—	28.—	78.—
„	„ 21st „ 31st	8.25	69.—	40.—	28.—	78.—

The total exports of oils amounted in the months of:—

		1921.	1920.
January	to kg.	98851	66865
February	„ „	81735	173851
March	„ „	102096	105497

According to an American patent of F. A. Mc. Dermott[1]) the oil of the agrumen fruits, especially of oranges and lemons, may be extracted in the following way:— The peels, freed of any flesh adhering, are cut into three or four parts and are dried at a comparatively low temperature, cautiously in the air, in such a way that as much water as possible may escape without any loss of volatile oil. This is possible because the essential oil is retained by the cell membranes, whilst the water can better diffuse through the membranes and then evaporate. The peels are then cut up further; sometimes they have again carefully to be dried, before they are submitted to steam-distillation in a vacuum, in a finely-ground condition. Comparative experiments have

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[1]) U. S. P. 1353169. *Perfum. Record* **12** (1921), 18.

demonstrated that the best results are realised when the peel was not only not stirred with water before the distillation, but when it had so far as possible been freed of any water it contained.

The thus-prepared, almost colourless oil is said to exceed in fineness (odour and taste) all products prepared by other known methods[1]). Since there is mostly a great preference for coloured oils, the disintegrated extreme skin of the fruit is for some time macerated in the distilled oil until the latter has assumed the desired characteristic colour[2]). According to this patent the oil can, further, be preserved for short or long periods and be protected in particular against oxidation by being mixed with one or 2 per cent. of olive oil or with 10 per cent. of absolute alcohol.

It will be very interesting to see whether this method will prove satisfactory in the long run. So far similar methods have not been able to replace the old-fashioned way[3]).

As regards Agrumen on the isle of Cyprus, see page 83 of this *Report*.

As regards Spanish Agrumen oils, cf. page 75 of this *Report*.

Bergamot Oil.—Early in November the prices began to fall rapidly under the pressure of a decreasing demand and of the commencing new harvest. The depreciation would have been still more marked, if large stocks had not remained in the hands of well-to-do speculating traders. Even at the present time this product is still much neglected; but the consumers begin with the present prices at least to display sufficient interest to take steps for satisfying immediate demands. Whilst about 14000 kg. were shipped in January 1920, the shipments of the same period of the current year only amounted to 4000 kg. A further diminution of the prices may be anticipated shortly.

The optical rotation of the bergamot oil, we learn from our expert, was in general high and exceeded in some districts 22°. The dryness of last year is supposed to account for this fact. Statements as to the ester content are unfortunately not available, so that we cannot form a clear idea of the quality of the oil.

The valuation of oil substitutes in cases, where odour is the chief question, is naturally a matter for the perfumer rather than for the chemist. Nevertheless the examination of such products is occasionally quite instructive, as we learnt again in the testing of an artificial bergamot oil about which our expert opinion was consulted. Of esters this oil contained, in addition to about 25 per cent. of terpinyl acetate, about as much glycerin acetate, that is to say, a compound which is altogether without influence on the odour. In spite of that we might not raise any real objection against the use of this oil, if the assumption did not appear justified that the manufacturer was anxious to provide for as high as possible a fictitious contents of fragrant esters; for the ester value would indicate 91 per cent. of linalyl or terpinyl acetate! We are, of course, not in a position definitely to say whether our assumption is correct; but it is in any case not altogether to be rejected. If we should be right, the addition made would be tantamount to an adulteration.

Much more "artificial" was another substitute of bergamot oil, as to which our opinion was likewise requested. In this case the product consisted to about 60 per cent. of glycerin acetate, *i.e.*, a useless ballast, and the rest was mainly the methyl ester of anthranilic acid. It is difficult to say whether the provider was thinking of anything in preparing this oil, but we can conscientiously certify that he has blundered gravely with

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[1]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 9. — [2]) See also Hood's *method of preparing orange oil, Report* 1920, 32. — [3]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 12.

his ingredients; for a mixture of glycerin acetate and the methyl ester mentioned bears very little resemblance to bergamot oil.

With respect to the physical and chemical properties of the bergamot oils produced in 1920 21 in Calabria, a memoir by A. Parrozzani[1] should be mentioned. We see from this paper and its tables that the oils had mostly a high specific gravity, yet not exceeding the normal limits in general, *viz.* d_{15° 0.8801 to 0.8874; that the optical rotation was in general higher than 22° (up to 37°); an that the solubility of the oil in alcohol was lower than it had been in the preceding year, but that this figure also remained within normal limits. (1 vol. of oil was soluble in 0.8 vol. of alcohol of 85 per cent. and in 0.5 vol. of alcohol of 90 per cent.). The first fraction of the distillate (one third of the oil), gave only in three cases twice as large a rotation as the oil. The ester content amounted to 30 to 40 per cent., in some cases to 45.76 per cent.

Parrozzani has evidently been experimenting also with oils which had been expressed at the beginning of the harvest from unripe fruit which the storms had brought down from the trees. That would help to explain the deviations from the normal in specific gravity, ester content and solubility which he observed, though it would not suffice to explain rotations of + 37°. So high values have so far only been found when the respective bergamot oil contained lemon oil or orange oil. The results of Parrozzani's study can, of course, not be utilised for the valuation of the bergamot oils of the trade in which we have to deal with average products.

Lemon Oil.—This important oil is still depreciating in value, and the end of the down grade movement can not yet be foreseen. The demand was especially weak in February, a month which, as the export statistics which we gave above will indicate, was exceptionally quiet in the market of essential oils. Rumours which became current again from time to time of a total stock exhaustion in the countries of consumption do not appear to have been justified; for the retrogressive price movement had not come to its end by March and a stronger demand was still in vain looked for.

It is well known that the properties of lemon oils depend much upon the season and upon the state of maturity in which the fruit are gathered[2]. According to A. Boake, Roberts & Co., Ltd.[3], the lemon oils prepared at the beginning of the season, that is, in December and January, possess the highest citral content and the highest optical rotation, as well as the lowest density and the relatively smallest amount of non-volatile residue. The yield of oil is, moreover, best in this season. In the measure as the fruit ripens, the content of citral in the oil diminishes and the proportion of waxy constituents increases. As a consequence the solid residue which, at the beginning of the season, will amount to about 2 per cent., may rise to 3 per cent. and more by May.

We have not been able to observe any particular regularity in this report. (Cf. *Report* November **1908**, page 63, as well as E. M. Chace, The Occurrence of Pinene in Lemon Oil. United States Department of Agriculture, Bureau of Chemistry, Circular No. 46, page 15 to 19 [30. X. 1909.]).

As regards the different lemon oils of Sicily we have another paper by Boake, Roberts & Co.[4] In a somewhat modified and expanded form we find there stated what

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[1] *Le proprietà fisiche e chimiche delle essenze di bergamotto prodotto in Calabria nella campagna agrumaria 1920—1921. Annali dalla R. Staz. Sperim. per l'industria delle essenze e dei derivati dagli agrumi* **1** (1921), 1. Reprint kindly sent to us. — [2] Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 16. — [3] *Drug and Chem. Markets* **7** (1920), 339. — [4] *Perfum. Record* **11** (1920), 249.

we could write years ago on the strength of personal observations and enquiries concerning the production of different sorts of lemon oil[1]). According to that firm, the citral content would be 4 per cent. for Acireale and Giarre oil, about 5 per cent. for Messina oil and 3.5 to 4 per cent. for Barcelona oil. Their figures for the optical rotation, which is particularly characteristic for the different kinds of oil, are:—oil coming from the district between Acireale and Giarre $\alpha + 59$ to $+60°$, oil from Giardini $\alpha + 62$ to $+63°$, and oil from Messina $\alpha + 57$ to $+59°$.

Lemon oil has recently been prepared also by the following method[2]) which differs from the previously used *"spugna"* and machine methods. The lemons are turned between two surfaces, the one concave, the other convex, which are set with small pins to scrape the skin of the fruit and to tear the oil-cells. A jet of water passes over the fruit and carries with it the products which have been liberated from the cells. This water is collected in suitable vessels; after a while the main bulk of the lemon oil will settle, clear for easy recovery, while the turbid portion of the liquid is purified by filtration.

Compared to the old *spugna* process the method seems to be inferior in so far as, according to P. Leone[3]), the treatment with water impairs the quality of the oil. Leone proved in the first instance that, in oils which he had shaken with 6, 20 and 40 times the amount of water, the specific rotation was constantly increasing whilst the density and the citral contents correspondingly diminished. The constants of the oil were very little affected, however, when the oil was shaken with water which had already been saturated with lemon oil.

The influence upon the quality of the oil of the water treatment can best be seen from the following table in which the constants of the oils, as prepared by the different methods from the same material, are reproduced.

Lemon oil prepared by	$d_{15°}$	$\alpha_{D20°}$	Citral content[4])	Evaporation residue
spugna process . .	0.8583	$+60° 20'$	4.25 per cent.	2.90 per cent.
water treatment . .	0.8576	$+60° 32'$	3.90 per cent.	2.95 per cent.

Leone recommends to make use, in the new method, only of water already saturated with lemon oil, since the quality of the product would then little be affected.

A. Guido[5]) has continued his research on the demonstration of adulterations in lemon oil. In the manner previously described[6]) he investigated the influence of alcohol of different concentrations upon the critical solution temperature. This temperature rises with increasing density of the alcohol, and with adulterated lemon oil to a greater extent than with the genuine oil. Especially with the higher fractions of his two samples of oil he observed a great difference between the two temperatures when using an alcohol of the highest suitable water contents. Guido therefore assumes that the application of a suitable alcohol (the constants of which were, in one case quoted by author, $d_{15°}$ 0.8436, 87.11 per cent. by vol.) would further improve the sensitiveness of this method.

In a further research Guido[7]) deals with the determination of the citral in lemon oil and in its fractions (by the method of Kleber) after treatment with solution of sodium bisulphite (100 grams of sodium bisulphite, 36 grams of sodium bicarbonate and 1000 grams

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[1]) Cf. *Report* April **1896**, 30; November **1908**, 62. Cf. also Chace, The by-products of the lemon in Italy, *Report* April **1910**, 64. — [2]) *Sulla essenza di limone estratta in presenza d'aqua. Estratto dal Giornale di Chimica Industriale ed Applicata.* November **1920**. Reprint kindly sent to us. — [3]) *Ibidem.* — [4]) Method of determination not stated. — [5]) *Sulle essenze di limone. Estr. Annali R. Stazione di Agricoltura e Frutticoltura Vol. V.* **1919**, p. 1. As per a reprint kindly sent us. — [6]) Cf. *Report* **1920**, 31. — [7]) *Distillazione frazionata e compositi carbonilici. Loc. cit.* p. 8.

of water). Starting from Tiemann's work¹) the author shows that, by shaking for 2 or 3 hours, the main bulk of the citral or of the aldehydes present in addition to citral can be removed with the aid of this solution from genuine, as well as from adulterated, lemon oil. In examining the separate fractions of the lemon oil samples he noticed that the differences found in the values of the citral content, before and after the treatment with bisulphite, were continuously increasing up to the eighth fraction. With the ninth fraction the difference became much smaller again, which Guido regards as an indication that the higher aldehydes had accummulated in this fraction. The author then compares the values for the genuine and for the adulterated oils and for the respective fractions in their variations and he arrives at the conclusion that the method which he had outlined and which is based upon the determination of the citral content of the separate fraction would also furnish the basis for an exact evaluation of lemon oils.

Mandarin Oil.—Although very high prices were paid last autumn for the fruit on the tree, the harvest seems to have been favourable, for the prices of mandarin oil which culminated by the end of April with 197 lire have since then been on a steady decline. At the present time the value of the article is about 80 lire, the demand being very small.

Orange Oil, Bitter.—This article was much neglected during the past six months and the prices dropped from about 90 lire in May gradually down to 28 lire. Buyers of larger quantities were absent since people were naturally waiting for the advantageous moment which, in our opinion, does not appear to have come yet.

Orange Oil, Sweet.—A glance at the table of prices on page 17 will show that this article, which likewise had reached its highest price of 185 lire in May of last year, also suffered from the general drop of prices, indicating that it was not simply the scarcity of the fruit available from the last harvest, but that the speculative policy of certain traders was also responsible for the high quotations. For some months already the product has completely been neglected, and the prices are down to 40 lire. In January of this year only 2500 kg. were exported, that is a quarter of the exports of the previous year for the same month.

On page 76 of this *Report* we mention some Spanish orange peel oils which D. B. Dorronsoro had investigated and described. Since we have ourselves in the last years repeatedly examined Spanish sweet orange oils, we may reproduce our own observations in connection with these researches of Dorronsoro. The oils were distinguished by a strong orange odour and a deep red-brown colour; of ten oils only one had a lighter colour. The constants varied between the following limits:— d_{15° 0.8511 to 0.8565; $\alpha_{D20^\circ} + 90^\circ$ to $+ 96^\circ 44'$; the α_D of the first 10 per cent. of the distillate in all samples higher (by 9° maximum) than the α_D of the original oils; n_{D20° 1.47348 to 1.47466; evaporation residue 3.4 to 11 per cent.; aldehyde (decylaldehyde)²) contents 1.2 to 2.7 per cent. (by phenylhydrazine method). The sap. v. found with one evaporation residue was 157.0.

These values agree on the whole with those of Dorronsoro. From the oils obtained in Italy the Spanish oils differ, apart from odour and especially from colour, partly

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¹) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 410. — ²) According to K. Stephan (*Report* October 1900, 29) sweet orange-peel oil contains only decyl aldehyde. Dorronsoro (*loc. cit.*) speaks erroneously of citral.

also by the higher specific gravity, the mostly lower rotation and the mostly higher dry residue. The differences are explicable by the degree of maturity of the respective fruit, and also by the mode of preparation of the oil. In Spain the completely-ripe fruit of red colour is used. It is turned by hand on a steel cone, which is provided with small projections, until all the outer skin has entirely been rubbed off. This skin, which contains the oil, drops into wooden boxes in the form of a wet flour; the flour is put in bags of camel hair which are placed between steel plates in a hydraulic press to obtain the oil.

The harvesting of the oranges takes place in the months November to March. The beginning of the harvest changes somewhat with the district. Use is made only of the sweet Spanish orange of which there are several species. In the opinion of our informant the oil production may be estimated at from 10000 to 15000 kg.

To all appearance Japan also has been entering upon the manufacture of agrumen oils. If two samples of orange oil, forwarded to us, should actually be characteristic of the Japanese product, however, the Italians need not fear this new competition; for both the oils proved to be useless. The one had the following qualities:— d_{15° 0.8561; $\alpha_{D20^\circ} + 76^\circ 22'$; α_D of the first 10 per cent. of the distillate $+92^\circ 6'$; evaporation residue 7.3 per cent. These values accord neither with those of sweet orange oil, nor with those of bitter orange oil. Above everything the rotation figure is too low. We gain in fact the impression that we are not dealing with a pure orange oil at all, and this all the more so, since the comparatively-large dry residue has not a waxy, but a fluid consistency. It looks as if the manufacturer had been making use of some fatty oil or mineral oil.

The other sample was colourless, a fact, which suggested, as did also the stale odour, a distilled oil, the purity of which was not quite beyond doubt either. The first ten per cent. of the distillate had a much lower optical rotation than the original oil, a fact, so far not observed in distilled orange oils. This oil cannot either be of any commercial importance, and we add the constants which we observed only for the sake of completeness:— d_{15° 0.8490; $\alpha_D + 92^\circ 52'$; α_D of the first 10 per cent. of the distillate $+87^\circ 30'$; soluble in 6 vol. and more of 90 per cent. alcohol with very slight turbidity.

Eucalyptus Oil.—As long as Australia does not remove the interdict placed on German productions, German firms cannot be expected to take into consideration the offers of representations of Australian firms which come from all sides. Spain is fortunately in a position to supply sufficient quantities of excellent globulus oil with a high content of eucalyptole. Promising experiments on the distillation of eucalyptus oils have recently been made also in Chile.

Two eucalyptus oil firms of Sydney and Melbourne have amalgamated to a company with a capital of 125000 £ which has its main plant in Balmain, Sydney¹). The company further contemplates to establish three new factories in Queensland for the preparation of the oil of *Eucalyptus citriodora*, of citronellal and further of citronellol. They further prepare eucalyptole, phellandrene, peppermint ketone (piperitone) and geranyl acetate, from *Eucalyptus Macarthuri*.

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¹) *Perfum. Record* **11** (1920), 361.

As regards the preparation of thymol, menthone and menthol from piperitone $C_{10}H_{16}O$, which, according to H. G. Smith and A. R. Penfold, is contained in the essential oils of many kinds of eucalyptus and in the oil of *Eucalyptus dives,* in addition to phellandrene, to the amount of 40 to 50 per cent., we have a long report by these authors[1]. Since the inactive racemic modification of piperitone, which is originally lævorotatory, is formed when the oil is heated at ordinary pressure, the natural lævorotatory piperitone is only obtained when exparated by distillation at strongly-reduced pressure. Such a piperitone purified with bisulphite possessed the constants: — b. p. 229 to 230° (not corrected, usual pressure), 106 to 107° (10 mm.); d_{20° 0.9348; α_D — 40.05°; n_{D20° 1.4837; semicarbazone, m. p. 219 to 220°; oxime, m. p. 110 to 111°; oxamino oxime, m. p. 169 to 170°; mol. refr. 46.49 (calculated for $C_{10}H_{16}O$ 45.82; the difference in the values is ascribed to the double bond)[2]. The oxidation of piperitone with potassium permanganate yielded among other products *iso*butyric acid. Since further the ketone could be oxidised to thymol and reduced to methone, the authors assume that piperitone is constitutionally a Δ^4-menthenone-3 or a Δ^1-menthenone-3[3].

By the oxidation of piperitone with ferric chloride in glacial acetic acid Smith and Penfold obtained 25 per cent. of thymol. By reducing the ketone by means of hydrogen they obtained menthone in almost quantitative yield (b. p. 208°; d_{20° 0.8978; $[\alpha]_D$ — 0° 15′; n_{D20° 1.4529; oxime, m. p. 80°; semicarbazone m. p. 156°). By treatment with sodium in aqueous-ethereal solution the menthone was further converted into inactive menthol (m. p. 34°). The reduction of piperitone with sodium or sodium amalgam in alkaline solution led to a bimolecular ketone $C_{20}H_{34}O_2$ (m. p. 148 to 149°). The authors believe that it will be possible to prepare from the abundant raw material both thymol in better yields and active menthol so as to satisfy medicinal requirements, on a large scale.

In the eucalyptus oils which contain piperitone R. T. Baker and H. G. Smith[4] found an alcohol corresponding to this ketone, which they called piperitol. A larger quantity of this piperitol they obtained from the oil of *Eucalyptus radiata,* Sieb. by removing the ketone from the piperitone fraction of b. p. 100 to 103° (10 mm.) by shaking with sodium bisulphite and further by fractionated distillation of the residue at a pressure of 10 mm. The piperitol prepared in this way (b. p. 95 to 96° (10 mm.); d_{20° 0.9230; α_D — 34.1°; n_{D22° 1.4760; mol. refr. 47.04; calculated for $C_{10}H_{18}O/\overline{1}$ 47.14) could be oxidised, by means of potassium dichromate, to piperitone (d_{15° 0.9390; α_D — 24.0°; n_{D20° 1.4832. It is noteworthy that piperitone has not conversely been converted so far into piperitol by reduction.

C. Kleber and W. v. Rechenberg[5] determined the cineole contents of eucalyptus oil by determining the solidification temperature of the respective oils and by calculations based upon their tables. In this determination, which is carried out in a double-walled refrigerator, if possible provided with a vacuum jacket, attention should be paid to the true solidification point, that is to say, the temperature at which crystalisation just begins or stops. This is best done by repeatedly remelting the solidified oil and by

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[1] Baker and Smith, *A Research on the Eucalypts.* 2nd ed., **1920**, p. 390. —

[2] Cf. *Berl. Berichte* **41** (1908), 1812. —

[3] The formation of *iso*butyric acid speaks for the 4-position of the double bond; according to Wallach (*Chem. Zentralbl.* **1912**, II, 923), however, Δ^4-menthenone-3 is not oxidised to thymol by boiling with ferric chloride in glacial acetic acid, contrary to Δ^1-menthenone-3. Assuming the authors to be correct, piperitone should then have the constitution of a Δ^1-menthenone-3. We should say, however, that l-piperitone is not identical with the dextrorotatory Δ^1-menthenone-3 with we have found in Japanese oil of peppermint, although many constants of the two substances approach one another closely (see *Report* Oct. **1910**, 97). There are possibly two modifications of the same substance. —

[4] Baker and Smith, *A research on the eucalypts especially in regard to their essential oils.* 2nd ed., p. 373. —

[5] *Journ. f. prakt. Chem. N. F.* **101** (1920), 171.

ascertaining the exact point by applying weak cooling. Pure cineole melts at + 1.2°; the less cineole the oil contains, the lower will be the solidification point. The authors have given a table of the solidification points of mixtures of cineole (pure cineole + hydrocarbon [pure, freshly-rectified oil of turpentine]) for a series of the usual concentrations, 65 to 100 per cent. of cineole. Since eucalyptus oil contains, in addition to cineole and the hydrocarbons, several percent. of oxygenous constituents — aldehydes and alcohols — they have determined the influence of these bodies by making additions to their mixtures of cineole. They observed that the solidification point was very little affected, raised or lowered, by these additions, and that the deduced values differed by 1 per cent. at the most from the true cineole percentage. The authors state that this method, which is distinguished by its great simplicity from all other methods, has always given very satisfactory results in the course of several years.

In oils which contain less than 65 per cent. of cineole the solidification method was likewise applicable with success, provided that the sample be mixed with the same amount of cineole before the determination.

Want of time has so far prevented our testing this method; we shall, however, revert to it.

As regards addition products of cineole and *o*-cresol comp. page 63 of this *Report.*

Fennel Oil. — As to Spanish fennel oils, cf. page 78 of this *Report.*

Oil from a species of Ferula. — From the fresh root of a kind of ferula *(Ferula copalensis?)*[1] which grows in Turkestan near Medeo, not far from Wjernyj (Semirjetchensk), E. Swirlowsky[2] obtained by steam distillation 2 to 2.3 per cent. of a greenish transparent oil which smelled of oil of turpentine and also of parsley and which possessed the following constants:—d_{17° 0.8650; $[\alpha_D] + 10.602^\circ$; n_{D20° 1.4760. The oil became colourless on standing.

The mother plant grows at an altitude of 6000 feet in considerable quantities and has a root, up to 3 kg. in weight like a horseradish, which above carries a bunch of coarse hair. When the root is lacerated, a milky sap exudes smelling of French turpentine.

Geranium Oil. — According to an English abstract of a French report[3], the genus *Pelargonium* comprises some 600 species[4], almost all of which have their home near the Cape. Since the beginning of the nineteenth century the geranium plant *Pelargonium odoratissimum*, Willd., has been cultivated near Grasse in the south of France[5]. In 1847 the plant was introduced into Algiers, at Chéragas; from there its cultivation spread gradually. Forty five years ago the *Pelargonium odoratissimum* was introduced into Corsica, in the Bastia and Ajaccio districts, and since 1880 *Pelargonium capitatum*, Ait., has also been cultivated on the island of Réunion. Algiers exported in 1904 63660 kg., in 1910 only 33800 kg., Réunion in 1900 9000 kg., in 1910 63000 kg. and in 1913 37000 kg. of geranium oil. The oil prepared in Grasse — in the last years it was only 1000 kg. annually — is said, in the report quoted, to be the most highly-esteemed (the Spanish oil is in reality the finest); at the beginning of this year it was sold at 280 fr.

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[1] This *Ferula*-species is not mentioned in the *Index Kewensis* up to 1910. — [2] *Berichte d. deutsch. pharm. Ges.* **30** (1920), 478. — [3] *Chemist and Druggist* **93** (1920), 1334. — [4] This figure does not agree with Engler *(Die Vegetation der Erde: Die Pflanzenwelt Afrikas, Bd. III, Heft 1, S. 708)* and is probably too high. — [5] Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 614.

per kg. The price of Algerian oil was 220 fr., and of Réunion oil 80 to 100 fr. per kg. By good farm-manuring the yield of the geranium plantations can much be improved. Thus France reaped 70000 kg. of leaves per hectare in well-manured plantations, whilst the yield on Réunion was only 25000 kg., from unmanured soil.

Since 1914 the Bureau of Plant Industry, United States Dept. of Agriculture, at Orlando, Orange County, Florida, has been experimenting on the cultivation of several varieties of the *Pelargonium odoratissimum,* Willd. G. A. Russell[1]) has reported on these experiments and especially on the species which give an oil most similar to the commercial geranium oil. It proved to be advantageous to put the slips at once into the open field (8000 plants per acre), and this in the months of January or February, after rain. The plants prospered on light, sandy soil and bore both dryness and moisture well, provided that the water could easily run off after rain. Some compound manure or artificial fertiliser seemed to improve both the yield in herb and the percentage of essential oil. The soil had to be tilled several times a year to remove the weeds. Under such conditions 16720 lbs. were reaped in the first year, 7618 lbs. in the second year, and 4499 lbs. of fresh herb per acre in the third year. So far as the oil was concerned it proved immaterial whether the cut plant was at once distilled, or whether it was left covered up for several days before distillation. More oil was, however, produced when the herb was cut after a sunny day, than when reaped after strong rain. In all cases the yield of geranium oil which amounted to from 1.35 to 9.33 lbs. per acre or to 0.051 to 0.082 per cent. was not very encouraging, and it would appear to be doubtful whether the cultivation of the geranium plant in Florida will ever prove profitable.

As regards Spanish Geranium oils, cf. page 77 of this *Report.*

Ginger Oil.—As regards ginger oil from the Philippine Islands, cf. page 85 of this *Report.*

Gouft Oil.—Under the name of gouft oil P. Jeancard and C. Satie[2]) describe the product of distillation of a plant, growing on the Algerian plateaux, which they do not further specify. The same oil, the mother plant of which, according to E. G. and A. Camus, is *Artemisia campestris,* L., *var. odoratissima,* Desf., has recently been investigated by Roure-Bertrand Fils[3]) who come to similar conclusions.

By contrast to the sheih or chieh oil (cf. p. 43 of this *Report*) the gouft oil had hardly changed after several years' storage and showed the following constants:—d_{15° 0.8763; α_{D15° —16°24′; soluble in 0.5 vol. of alcohol of 96 per cent. at 15°, becoming strongly turbid on further addition of alcohol; acid v. 0.94; ester v. 29.87; sap. v. 30.81; after acetyl ester v. 41.07; total alcohol (calculated as $C_{10}H_{18}O$) 11.65 per cent.; free alcohols (calculated as $C_{10}H_{18}O$) 3.44 per cent. Steam distillation of the oil yielded 80 per cent. of a colourless oil of the following properties: d_{17° 0.8524; α_{D17° —17°44′; soluble in 1 vol. of 96 per cent. alcohol and in 16 vol. of 80 per cent. alcohol, no turbidity on further addition of alcohol; acid v. 0; ester v. 9.33; sap. v. 9.33; ester v. after acetylation 39.20; total alcohol (calculated as $C_{10}H_{18}O$) 11.11 per cent.; free alcohol 8.45 per cent. The distillate gave at normal pressure the fractions:—(1) below 105°, 10 g., $d\frac{15^\circ}{15^\circ}$ 0.8539; α_{D15° — 19°48′; (2) between 165 and 170°, 8 g., $d\frac{15^\circ}{15^\circ}$ 0.8539;

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[1]) *Journ. Americ. pharm. Assoc.* **10** (1921), 19. — [2]) Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. III., p. 667. — [3]) Bull. Roure-Bertrand Fils, avril **1920**, 27.

α_{D15° −17°52′; (3) 170 to 175°, 2 g., $d_{15^\circ}^{15^\circ}$ 0.8530; α_{D15° −15°; residue 5 g. The first two fractions contained *l*-*α*-pinene and probably nopinene. On the oxidation of the last fraction the smell of citral became distinctly noticeable; geraniol was therefore present.

Jasmine Oil.—The yield of jasmine oil is known to be greater with the enfleurage method than with extraction by volatile solvents[1]. A. Hesse, and later Charabot and Gatin, have explained this fact by the assumption that the plant contains a glucoside, the decomposition of which continually liberates fresh portions of the essential oil during the enfleurage. This assumption is supported by the experiments of J. Nivière[2]. When jasmine flowers are treated with acids or enzymes before extraction by means of solvents, the yield of essential oil realised is increased. The essential oil thus obtained differs slightly from the product gained from flowers which had not been treated previously.

Juniper Berry Oil.—As regards Spanish juniper berry oil see page 81 of this *Report*.

Oil from the Wood of Juniperus Oxycedrus.—By treating the oil of *Juniperus oxycedrus*, L. with the respective halogen hydrides, R. Huerre[3] obtained the dihydrochloride and the corresponding dibromo- and diiodo-compounds of cadinene.

The bodies obtained were identical with those which Wallach[4] had prepared from cadinenes of various origins. From the quantity of the diiodo-product obtained the author calculated an average cadinene content of the oil of 21.11 per cent., maximum 30.59 per cent.

Oil from the Berries of Juniperus phœnicea.—E. Puxeddu and F. Vodret[5] have examined the little-studied[6] oil of *Juniperus phœnicea*. From the apparent fruit, still green, which had been collected in December on the south coast of Sardinia they obtained by steam distillation 1.60 to 2.25 per cent. and 2.48 to 2.50 per cent. of an essential oil, according as they distilled the berries directly or after maceration with water. The colourless, clear oil, wich turned rather yellow in the light, had an agreeable aromatic odour reminding of oil of turpentine when rubbed on the hands; it tasted like camphor and had the following constants:—d_{15° 0.8658; $[\alpha]_D$ +16.84°; n_{D20° 1.4675; insoluble in 80 per cent. alcohol, soluble in 16 vol. 90 per cent. alcohol at 27°; acid v. 2.49; ester v. 12.01; sap. v. 14 to 15; ester v. after acet. 35; total alcohol (calculated as $C_{10}H_{18}O$) 20.9 per cent.; iodine value (Huerre)[7] 285.53; bromine value 264.55.

The distillation at reduced pressure (70 mm.) yielded the fractions:—1. 120 to 122°, 27 per cent.; 2. 122°, 30.5 per cent.; 3. 123 to 131°, 11 per cent.; 4. 132 to 157°, 4.4 per cent.; 5. 158 to 198°, 11.3 per cent. Fractions 1, 2, 3, redistilled together at 30 mm., gave fractions 75 to 80° and 81 to 92°. The fraction 75 to 80° was by further distillation separated into three fractions:—74° (d_{25° 0.8543; $[\alpha]_D$ +23.94°; n_D 1.4644); 75°, and 76 to 80°.

Ladanum (Labdanum) Oil.—The distillation of a resin from *Cistus ladaniferus*, L., coming from the Esterel mountains, Southern France, gave, according to Roure-Bertrand Fils[8], 0.06 per cent. of a golden-yellow essential oil of not unpleasant odour

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[1] Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I., p. 264. — [2] *Bull. Soc. chim.* IV. 27 (1920), 862. — [3] *Journ. de Pharm. et Chim.* VII 23 (1921), 81. — [4] *Liebig's Annalen* 252 (1889), 150, 151. — [5] Cf. *Report* April 1913, 69; *Report* April 1914, 66. — [6] *Gazz. chim. ital.* 50 (1920), II. 245. — [7] *Journ. de Pharm. et Chim.* 19 (1919), 216. — [8] *Bull. Roure-Bertrand Fils*, October 1920, 3.

and the following constants:—d_{20° 0.9033; α_{D67° — 12°10′; $n_{D12.5^\circ}$ 1.4800; acid v. 3.7; ester v. 18.67; sap. v. 22.37; soluble in 0.5 to 5 vol. 90 per cent. alcohol1)。 The distilled waters yielded on extraction with petrolether 0.02 per cent. of an oil of a still finer odour than the original and of the following constants:—$d_{17.5}$ 0.9755; α_{D17° — 2° 40′; acid v. 18.67; ester v. 22.40; sap. v. 41.07; soluble in 0.5 and more vol. 90 per cent. alcohol.

Concerning the various species of cistus, from which the ladanum resin is obtained, A. Camus2) has published an extensive research in which he deals in particular with the botanical characteristics of *Cistus ladaniferus*, L. and *Cistus monspeliensis*, L. Of the former plant, which occurs almost all round the Mediterranean, three subspecies are known:—*albiflorus*, Dunal, *maculatus*, Dunal and *stenophyllus*, Dunal. As the different kinds of cistus have characteristic forms of hair, it is possible to determine the botanical origin of the ladanum resin accurately from the hair which are always found in the resin.

Lavender Oil, French.—The general decline in prices has naturally affected also the lavender oil market, and though at present prices are demanded which must still be considered extraordinarily-high, it is clearly apparent that the obstinacy of the producers, who last autumn insisted upon prices of 275 and even 300 fr. for their finest qualities, will not long hold out in view of the actual state of affairs. At the present moment the producers demand for a product with more than 50 per cent. of ester 165 fr., with 40 per cent. of ester 120 fr. (our own lavender oil extra) and with 35 per cent. of esters (so-called "Mont-Blanc") 115 fr. It need hardly be said that with these prices no more than the most indispensable quantities are bought for current needs, and we should not be surprised if, considering the little-satisfactory aspect of the industry of perfumes and soaps, large stocks would have to be taken over into the new harvest.

According to news from England3) the cultivation of lavender has seriously diminished near Mitcham. In the whole county of Surrey only 10 acres are still said to be under lavender cultivation.

A brochure recently published by the French Ministry of Commerce4) deals with the extension and the cultivation of lavender in France. The brochure is based upon the classification of Jordan who distinguishes two subspecies of *Lavandula officinalis*, L., *Lavandula angustifolia (fragrans)* and *L. delphinensis*. Whilst *L. angustifolia* likes light and dry ground, *L. delphinensis* thrives better in shaded and moist localities. Intermediate between these two species are, however, numerous transition forms. Both the genuine lavender and the spike lavender require calcareous soil, by contrast to *L. Stœchas*, L., which prefers a silicious soil. *L. officinalis* was found by A. Humbert at an altitude of 700 m. in sunny spots in the Département Aveyron to the north of the Causses and south of Millau, but also at much lower altitude (400 m.) and on slopes looking north in the north of the Ventoux5). Near Rouy, in the Dauphiné, the plant still occurred at an altitude of 1800 m., whilst as a rule near the Ventoux in the neighbourhood of Die, and at Veynes in the Hautes Alpes, 1500 to 1600 m. are the extreme altitude limits of this plant.

Humbert questions the view that *Lavandula delphinensis* occurs only at high altitudes. Thus *Lavandula fragrans* grows on the southern slopes of the Glandasse up to a height

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1) The oil strongly resembles the oil of *Cistus ladaniferus* which we examined; cf. Gildemeister and Hoffmann, *loc. cit.*, vol. III, p. 179. — 2) *Ibidem.* — 3) *Perfum. Record* **11** (1920), 257. — 4) *Ibidem* **11** (1920), 251. — 5) Cf. Gildemeister and Hoffmann, *loc. cit.*, vol. III, p. 426 (map).

of 1500 m. on warm and sunny spots, whilst *L. delphinensis* thrives at lower altitudes on woody slopes.

One of the largest centres of the lavender industry is near Sault de Vaucluse, 12 km. southwest of the Ventoux. Here both the wild-growing plant and the plant cultivated in the fertile valleys of Sault are being utilised.

The spike lavender, *Lavandula latifolia,* Vill., is as widely spread in the south of France as the true lavender. The former, however, thrives only at lower altitudes in regions facing north, as in the territory between Millau and Roque Ste. Marguerite and Montpellier-le-Vieux or near Buis-les-Baronnies.

As the lavender oils are differentiated both by their contents of linalylacetate and by the fineness of the aroma, the question has arisen whether the character of the oil depends merely upon the botanical variety or also upon ecological and other factors. As regards *L. officinalis* and *L. latifolia,* Humbert considered it to be established that the differences between the two plants, due to their botanical origin, were also decisive for the peculiarities of their essential oils. More difficult, and not yet sufficiently clear would be the question in the case of the numerous sub-species of *L. officinalis.* Light and moisture have a strong influence upon the formation of morphological modifications. On the other hand the differences in the soil, the climate and the altitude are not without importance for the character of the oil. The same kind of lavender which, in one district, yields an oil of a special character, need not necessarily give exactly the same oil on another spot.

It has, further, long been known that climate and season and their variations influence both the quality and the quantity of the essential oils of lavender. In wet years the yield of oil, as well as the ester contents, are low. From cultivated lavender we might obtain twice as much oil as from the wild plant. 100 kg. of fresh cultivated flowers are said to have given 1 kg. of oil.

The lavender plant is very common in the mountains of Morocco, on the Atlas. The variety which is there found growing in hardy shrubs¹) yields an oil which is highly esteemed and which is prepared by water distillation in a kind of peripatetic fashion²).

We have recently been consulted respecting an oil of lavender which had been sold by a Munich firm as "genuine and pure", but which had proved useless when applied in the keramic industry. The examination showed that we had to deal with an oil which was either strongly adulterated, or altogether an artificial product. It had the following constants:—d_{15° 0.9242; $\alpha_D - 0^\circ 16'$; not completely soluble in 10 vol. of 70 per cent. alcohol; acid v. 0.7; ester v. 94.3 = 33.0 per cent. of ester calculated as linalylacetate; sap. v. 95.0; acid v. II 89.6; difference between sap. v. and acid v. II 5.4; difference of the ester value in fractionated saponification 27.1; glycerin acetate test, positive. The oil is evidently much too heavy, of too low a rotation and of quite insufficient solubility. From the excessive difference of the ester values which were found in the fractionated saponification (normally 5 at the most) we presume an addition of terpenylacetate to an extent which, we deduce from former observations³), probably amounted to 15 or 20 per cent.

A further possible adulterant would be glycerin ester. This seems to have been used more sparely; for the analysis would indicate only 3 or 4 per cent. of glycerin

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¹) It is not clear whether *Lavandula vera* or *L. spica* is spoken of; both occur in Northern Africa. The term "hardy" suggests *L. spica.* — ²) *Rev. des produits chim.* 22 (1919), 647. — ³) Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. III, p. 70.

triacetate which, however, would still be interpreted into some 8 to 10 per cent. of linalyl acetate. Since the ester value of the oil suggests altogether 33 per cent. of linalylacetate there remain, after deducting at least 15 per cent. of added terpinyl acetate and further 8 per cent., probably of glycerin triacetate, only 10 per cent. of real linalyl acetate.

When we consider that pure lavender oil contains at least 30 per cent. of linalyl acetate, we have to conclude that the oil in question consisted to one third, at the best, of lavender oil whilst the rest was compounded of the esters mentioned and some other additions which partly must be very sparely soluble, since the whole oil was very difficult to dissolve.

It need hardly be stated that this oil was once more one of the so-called cheap oils; the price demanded was about half of what the producer would expect for lavender oil.

Lavender Oil, Italian.—Italian lavender oils are known to possess a low contents of esters (20 to 32 per cent.)[1]. This may be the chief reason that this oil is only manufactured in relatively-small bulks (up to 3000 kg. annually), although the lavender plant grows abundantly in the mountainous districts of northern Italy, especially in the valleys of Stura and Gesso, in the valley of Aosta and in the Maritime Alps. According to an English journal[2] an oil coming from the Stura valley contained 37 per cent. of lynalylacetate, that is to say, a higher ester percentage than is usual. If the author, on the strength of this fact, considers Italian lavender oils to be rich in esters, this may have to be taken by comparison to English lavender oils which possess an ester contents ranging from 5 to 10 per cent. The statement would not be correct without this qualification, since French oils frequently contain 40 to 50 per cent. and even more of lynalylacetate, as will be known.—One firm is said to have started cultivating lavendar in Italy. We shall have to wait a year or two for the results of these experiments.

Lemongrass Oil.—With respect to lemongrass oil from the Philippine Islands see p. 85 of this *Report*.

Marjoram Oil.—As regards Spanish marjoram oils see p. 82 of this *Report*.

Mustard Oil.—Samples of milk to be kept for analysis may, according to P. Post[3], be preserved by means of mustard oil, 20 drops per litre. Mustard oil is preferable to the potassium dichromate frequently used for this purpose, because it can, if necessary, be removed again without detriment before the milk analysis, and because its presence does not exclude the determination of the acid and of the freezing point. The catalysis number can, however, not be determined in milk to which mustard oil has been added. Post describes how the mustard oil is to be removed from the sample, before the determination of freezing point, milk sugar and albumin.

Oil of Myristica Otaba.—The seeds of *Myristica Otaba*, Heim, a tree growing in the mountains of Columbia at an altitude of 5000 ft., have been studied in the Imperial Institute[4] of London. The steam distillation of the seeds, which resemble nutmeg, yielded 7.2 per cent. of a colourless oil of the following properties:—$d_{15^\circ}^{15^\circ}$ 0.894; $\alpha_D + 79.44^\circ$; n_D 1.502; acid. v. 13.6; ester v. 0; ester v. after acetyl. 20.0; soluble in 16 vol. 90 per cent. alcohol.

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[1] Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 435. — [2] *Perfum. Record* 12 (1921), 5. — [3] *Pharm. Weekblad* 58 (1921), 131. — [4] *Bull. Imp. Inst.* 18 (1920), 168.

W. F. Baughmann, G. S. Jamieson and D. H. Brauns[1]) have examined an otaba butter likewise coming from Columbia. The fat contained up to 9.3 per cent. of a pale-yellow essential oil (d_{20° 0.89067; $\alpha_D - 32^\circ$; n_{D20° 1.4180). The distillation of 90 g. of this oil yielded the following fractions:—(1) 126 to 129° (13 mm.), 16.1 g.; (2) 134 to 137° (15 mm., the pressure was the same for the other fractions) 31.7 g.; (3) 138 to 142°, 10.6 g.; (4) 142 to 147°, 8.4 g.; (5) 147 to 175°, 3.0 g.; (6) 176 to 190°, 2 g., the residue (18.0 g.) turned crystalline on standing. The molecular weight of the second fraction was 204, in agreement with that of a sesquiterpene $C_{15}H_{24}$. All the fractions gave with glacial acetic acid and concentrated sulphuric acid the cadinene colour reaction. The authors hence assume that the essential otaba oil consists largely of sesquiterpenes.

The investigations indicate that the two otaba oils differed materially from one another. So far this difference has not been explained.

The value of the fat of the otaba fruit (American nutmeg or macebutter) as a remedy against skin diseases is mainly due to its contents of essential oil which is credited with germicide properties.

Niaouli Oil.—We have succeded in securing a small consignment of this oil which is much sought for in the manufacture of various pharmaceutical products, and we have reason to believe that the war-time dearth of this material has now completely been overcome.

Orange Blossom Oil.—Owing to the unusually-high prices the demand for bigarade oil was very slight, and the market showed at the beginning of September a decidedly weak tone, so that prices began to crumble. There happened about December 20 a fall of temperature, such as the south of France had not experienced for many a year. The thermometer went down to —9 degrees C., and a large portion of the shoots of orange trees were completely ruined. So far as can be seen at the present time the crop of orange blossoms will this year, at the very best, amount to a quarter of the normal yield. The orange trees offer a sad spectacle, because the damage done by the cold has been increased by the subsequent prolonged drought. Prices are talked of which are really fanciful, 30 fr. per kilo! The syndicate *(Société coopérative des producteurs)* has started a new factory in Vallauris to work up the total flower harvest, so that none, or only few flowers, would be left to the manufacturers at Grasse. The injury to the trees is so great that it will be felt at the next two harvests. Strongly-blended neroli oil of the last harvest has been paid 10000 fr. per kg., it is reported, in view of the conditions at Grasse.

The statistics, which *"La voix du peuple"*, Grasse, of January 8, 1921, publishes, will indicate the manner in which the prices have risen within the last few years. The kilogramme, of orange blossom fetched, in the years 1904 to 1917, 0.49 to 1.30 fr.; in 1918 the price was 1.70 fr., in 1919 2.25 fr., and in 1920 11.20 fr. per kg.

In Morocco the preparation of orange-blossom water has developed into a house industry. 1 kg. of orange blossom cost 1.4 to 1.75 fr. In the year 1915, 1187 kg. of orange-blossom water were exported to France, England and Spain[2]).

It is rather astonishing that Morocco does not push the orange-blossom distillation more than is done at present.

As regards Spanish orange-blossom oils cf. page 77 of this *Report.*

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[1]) *Journ. Amer. chem. Soc.* **43** (1921), 200. — [2]) *Rev. des produits chim.* **22** (1919), 647.

Orris Root Oil.—Recent reports from the orris root market of Florence indicate that all business transactions have come to a complete standstill, and that consequently the prices have been yielding considerably. As there is for the present little chance of a revival in the trade, we may look forward to further price reduction, unless prevented by the change in the Italian valuta.

We have fully taken up again the distillation of orris root oil, and the demand for our concrete orris root oil as well as for the *liquid tenfold quality,* has proved that the two kinds are equally highly esteemed in our country and abroad, and that their want has seriously been felt everywhere during the war.

Pagoda Grain Oil.—Under the name of *"Essence de Blé des Pagodes"* Roure-Bertrand Fils[1]) received from Annam a sample of an essential oil, the botanical source of which has not yet been identified. The oil which had a sharp burning taste, somewhat like orange-peels, and reminded in its smell first of palma rosa or ginger grass oil, and then distinctly of caraway oil, had the following constants:—d_{20° 0.9182; $\alpha_{D18^\circ} + 58^\circ 40'$; n_{D20° 1.4870; soluble in 1 vol. and more of 80 per cent. alcohol and in 2 to 4 vol. of 75 per cent. alcohol, insoluble in 70 per cent. alcohol:—acid v. 1.87; ester v. 9.33; sap. v. 11.20; ester v. after acetylation 130.67; total alcohol (calculated as $C_{10}H_{18}O$) 39.83 per cent., free alcohol 37.27 per cent. Nitric acid attacked the oil slowly in the cold; sulphuric acid decomposed it and coloured it brown.

30 g. of the oil distilled at 735 mm. gave the following fractions:—(1) 174 to 179°, 6 g.; $d_{15^\circ}^{15^\circ}$ 0.8554; $\alpha_{D15^\circ} + 95^\circ 22'$; (2) 184 to 202°, 5 g.; $d_{15^\circ}^{15^\circ}$ 0.8809; α_{D15° $85^\circ 2'$; (3) 202 to 212°, 3 g.; $d_{15^\circ}^{15^\circ}$ 0.8809; $\alpha_{D15^\circ} + 64^\circ 40'$; (4) 212 to 222°, 10 g.; $d_{15^\circ}^{15^\circ}$ 0.9479; α_{D15° $45^\circ 20'$; (5) 222 to 226°, 3 g.; $d_{15^\circ}^{15^\circ}$ 0.9524; α_{D15° $31^\circ 20'$; residue 3 g. Smell and physical constants of the first two fractions suggested *d*-limonene; the fourth fraction very probably contained some geraniol. Coumarine aldehyde seemed also to be present.

Palm Kernel Oil, Essential.—We commented in our *Report* of 1918, on page 38, on an essential palm kernel oil. As regards ketones we could only establish at tha time the presence of methyl-*N*-nonylketone. From the constituents of lower boiling points we could not obtain any semicarbazone of definite melting point, and we could only assume that we were dealing with a mixture of methylamyl ketone and methylheptyl ketone.

A further examination has confirmed this assumption. In the fractionated distillation of the fatty acids of palm kernels we obtained a first portion which, separated from the acid constituents by means of soda, smelled strongly of the lower methyl ketones. From this we isolated the following fractions (4 mm.):—(1) 30 to 45° 1 g.; (2) 45 to 55° 1 g.; (3) 55 to 60° 10 g.; (4) 60 to 87° 28 g.

Fraction 1 had indeed the characteristic smell of methylamylketone, but the quantity was too small to obtain a semicarbazone of a well-defined melting point. From the first portions of fraction 3 we obtained a ketone (6 g.) distilling between 56 and 57,5° (4 mm.) 1 g. of this was mixed with semicarbazide hydrochloride; after recrystallisation from alcohol it melted between 118 and 119°. The semicarbazone of methyl-*n*-heptylketone from clove oil melted at the same temperature, likewise did a mixture of the two semicarbazones.

Patchouli Oil.—Several larger consignments of patchouli leaves have been worked up within the last months in our factories so that we are again in a position

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[1]) *Bull. Roure-Bertrand Fils,* April 1920, 32.

to offer our own distillate of patchouli oil. This fact will be welcomed by all connoisseurs, since the oils from abroad are known not to satisfy more than the most moderate requirements as to finesse and intensity of the odour.

Pennyroyal Oil. — G. M. Beringer[1] reports on a commercial product of pennyroyal oil (d 0.884) which had been adulterated with 50 per cent. of alcohol.

Peppermint Oil, American. — For many months the well-situated planters and buyers of American peppermint oil in the west of America would not listen to moderate prices. Finally, however, a tendency towards decline set in which has not come to a stop yet. Already in November 1920 one could occasionally meet with smaller speculators ready to sell, although the market was still kept at 6 dollars per lb., rightly recognising that collapse was approaching. They went down to 5 dollars. Since then the market price has gradually sunk to 2.75 dollars per lb., and one can easily make an estimate of the sums which have been lost over this fall of 50 per cent. Only a few superior assortments were able to maintain higher quotations. Among the stored supplies, the existence of which was only revealed by the collapse of the market, there are said to have been consignments which must have cost the producer at least six dollars per lb.

For the market over here even the present price is not quite suitable yet once more to draw attention to the American oil without which we have had to do for nearly 4 years. For the present we shall be able to content ourselves with the excellent sorts prepared from Japanese peppermint oil, for the improvement of which we are continuously striving.

The yield of the peppermint harvest of the year 1920 will, it is estimated[2], be by about 30 or 35 per cent. larger than that of the preceding year. In 1919 some 12000 to 13000 acres under cultivation gave 260000 lbs. of oil. For the year 1920 we might, therefore, reckon on 351000 lbs. of oil. The annual consumption of peppermint oil amounts to from 300000 to 400000 lbs.

The formation of a trust and the fixation of a definite price were proposed at a meeting of the American peppermint planters of the United States. No agreements as to prices were arrived at, and the proposal was not accepted.

Peppermint Oil, Chinese. — So far there have been few investigations of Chinese peppermint oil[3]. An oil recently examined by Shinosaki[4] gave the following constants: — $d_{25^{\circ}}$ 0.9091; α — 35° (in chloroform); $n_{D25^{\circ}}$ 1.4627; S. V. 29; E. V. after acetylation 233; free alcohol (calc. as menthol) 70.57 per cent.; bound alcohol (calc. as menthol) 8.08 per cent.; menthone 12.88 per cent. The oil was light-brown in colour and had a disagreeable smell and a bitter taste.

Peppermint Oil, Italian. — According to an article by E. C. Bellini[5] the peppermint plant is cultivated in Italy especially in the provinces of Turin (near Pancalieri, Vigone, Ceretto di Carignano and Lombriasco) and in the province of Padua, on an area of 100 or 110 hectares. The article mentioned brings a fairly-general description of

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[1] *American. Journ. Pharm.* 92 (1920), 460. — [2] *Industrie- u. Handelszeitung*, 22. IX. 1920, p. 1474. — [3] Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 549. — [4] *Journ. chem. Ind.*, Tokyo 22 (1919), 458. From *Bull. Roure-Bertrand Fils*, April 1920, 124. — [5] *La Revista Ital. delle Essenze e Profumi.* From *La Parfum. Française* 2 (1920), 12.

the botanical characteristics, the cultivation, the diseases and the reaping of peppermint, but hardly anything of novelty to our readers. We therefore content ourselves with this reference.

Peppermint Oil, Japanese.—Final statistics concerning the exports of peppermint oil and menthol in the past year have now been published. According to these statistics the weights and values of the last three years were the following:—

		1918	1919	1920
peppermint oil	kin	214 635	409 199	313 630
	value in yen	549 716	1 307 113	1 812 366
menthol	kin	237 311	239 973	370 470
	value in yen	1 544 307	2 546 898	5 489 815

Thanks to the sustained support by the banks the numerous holders of large and dearly-bought stores in Japan, commanding more or less substantial capital, have for a long time been able to resist any price reduction with some success. In the main trade centres of Europe, especially in London, large stores of the oil remained in the hands of speculators, and thus it came about that people could occasionally buy more profitably in London or in Hamburg than in the country of production. The actually-existing high prices are in any case to be considered artificial. There are hardly any buyers in Japan; yet the holders of oil stock will not yield. Somewhat reduced prices are accepted only for postponed shipment. The still unsold stores are estimated by our experts at about 1700 cases of peppermint oil and the same quantity of menthol. Of these 800 cases of peppermint oil and 500 cases of menthol are reported to be in the hands of a single speculator who is not inclined, it is said, to part with his stock at present prices which may be attributed to the want of demand. Some day a reversion will have to set in, nevertheless. It is satisfactory that the stocks which, a few months ago already, were in the hands of some Hamburg profiteer firms of dubious character, who opposed any reduction in prices, have now passed into the consumers hands. A nice bit of money has been lost over these transactions!

According to Utz¹) peppermint oil gives the following colour reactions. A mixture of 1 g. of peppermint oil with 5 cc. of absolute alcohol, a few drops of furfural and a few cc. of hydrochloric acid (d 1.9) turns dark bluish-green when heated. When we replace the absolute alcohol of the mixture by glacial acetic acid, the red colour appears already in the cold and turns more intense on heating. 1 cc. of peppermint oil and 5 cc. of absolute alcohol and stannous chloride gave no colour change in the cold. On heating the mixture, however, a beautiful red colour became apparent, reminding of the sesame oil reaction of Baudouin and Soltsien²). The same phenomenon was observed when glacial acetic acid was substituted for absolute alcohol in the mixture.

Utz points out at the end of his communication that this reaction is not of any decisive importance.

We should ourselves like to emphasise once more, that such colour reactions are useless for the evaluation of essential oils.

According to Heinz³) peppermint oil stimulates the activity of the cells of the liver into an increased production of gall. Observations made on fair-sized animals, brings little more than a repetition and confirmation of formerly established facts.

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¹) *Deutsche Parf. Ztg.* **6** (1920), 208. — ²) *Chem. Revue Fett- u. Harzind.* **13** (1906), 138. — ³) *Therap. Halbmonatsh.* **34** (1920), 356.

rabbits and cats, always led to the same results. When the peppermint oil was introduced into the stomach, or subcutaneously or intravenously, the gall bladder was much expanded; its contents increased four and even eightfold and turned very fluid and clear, of a beautiful green colour, without showing any mucus or solid constituents. There was every indication that neither the red blood corpuscles nor the liver itself had detrimentally been affected by the remedy. After large doses of peppermint oil, introduced subcutaneously or intravenously, the gall taken from the bladder smelled strongly of peppermint oil. Heinz hence concludes that the oil has a special chemical or physico-chemical affinity to the liver cells or to the lipoid bodies of the liver, with especial regard to the gall secretion.

It was further shown that the gall, abundantly produced under the influence of peppermint oil, is able to soften gall stones, at least lecithine stones.

Heinz has also found peppermint oil an efficient remedy in some cases of cholelithiasis and he recommends to apply the oil in the form of tabloids of 0.0125 g. of oil (periodically, daily six to twelve tabloids).

As regards Spanish peppermint oil, cf. page 78 of this *Report*.

Oil of Perilla nankinensis. — Some years ago[1]) we described the oil of *Perilla nankinensis,* Decne. *(Perilla arguta,* Benth.; *Ocimum crispum,* Thunb., *Labiatæ)* which Semmler and Zaar[2]) had been investigating. We recently succeeded in finding l-*limonene* in the first portion of the distilled oil. As perilla aldehyde is based upon the skeleton of limonene, it was natural to presume the presence of this hydrocarbon in the oil itself. After separating the aldehydic and alcoholic constituents by the usual methods there remained an oil containing terpene and sesquiterpene from which a fraction of b. p. 48 to 60° (4 mm.) could be isolated. Distilled at ordinary pressure it possessed the constants: — b. p. 176 to 180°; $\alpha_D - 87.5°$. The tetrabromide prepared in the usual way melted after repeated recrystallisation from acetic ester sharply at 104°, and this melting point was not depressed by adding some *l*-limonene tetrabromide of known origin. The oil contains about 9 per cent. of this *l*-limonene. We further succeeded in isolating a fraction of b. p. 114 to 116° (4 mm.) which solidified already in the recipient. Dried on filter paper it formed long, hard, colourless needles of m. p. 128° and of a peculiar smell, recalling celery and parsley. The quantity available was unfortunately too small to carry our investigation further.

S. Furukawa and Z. Tomizawa[3]) have investigated the formation and the constitution of the essential oil of *Perilla nankinensis,* Decne. The abstract quoted does not refer to the fundamental work of Schimmel & Co.[4]) and of Semmler and Zaar[5]) which had already established and explained the constitution of the main constituents of the oil and of its derivatives. There is new information in the physiological part of the Japanese paper. The oils distilled from the fresh plant in different stages of their development indicated that the aldehyde percentage increased gradually, till the end of the bloom, at the expense of the esters, whilst the oils prepared from dry plants showed the inverse behaviour. In order to decompose the glucosides of the green plant and to convert them into oil it is necessary to prepare the enzyme and, therefore, to dry the plant at a low temperature. The chemical portion of the paper

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[1]) Cf. *Report* October **1910**, 146. — [2]) *Berl. Berichte* **44** (1911), 52; *Report* April **1911**, 93. — [3]) *Journ. chem. Ind.*, Tokyo **23** (1920), 342. From *Journ. chem. Soc.* **118** (1920), I. 750. — [4]) *Report* October **1910**, 146. — [5]) *Berl. Berichte* **44** (1911), 52; *Report* April **1911**, 93.

Novel is, however, the preparation of two stereoisomeric oximes. It is not stated, however, how the α- and β-compounds were separated from one another. The results of the investigation are summarised as follows:—The essential oil contained 20 to 30 per cent. of *l*-limonene, 44 to 57 per cent. of perilla aldehyde (b. p. 237°; d_{15° 0.9675; $[\alpha]_D - 145.8^\circ$) and some α-pinene. The α-anti-aldoxime (m. p. 102°) of this aldehyde was 2000 times as sweet as sugar, and 4 to 8 times as sweet as saccharin. The β-syn-aldoxime (m. p. 129°) was not sweet, which is strange. Of new derivatives were prepared the oxime hydrochloride (m. p. 114°) and the amide of perillic acid (m. p. 164 to 165°).

Petitgrain Oil.—As regards Spanish petitgrain oil, see page 76 of this *Report.*

Pichurim Bean Oil.—Pichurim bean oil, which so far had only once been examined by A. Müller[1]) in 1853, has been studied by Roure-Bertrand Fils[2]). From the disintegrated seeds of *Nectandra puchury major,* Nees, also called *Ocotea puchury major,* Mart., a species of the lauracee, which is a native of Southern Brazil, he obtained by steam distillation 2.3 per cent. of a yellow-greenish oil of a peculiar smell and of the following properties:— d_{17° 1.0396; $\alpha_{D16^\circ} - 4^\circ 54'$; n_{D16° 1.5180; soluble in 90 per cent. alcohol, in 3 vol. and more 80 per cent. alcohol and in 12 vol. and more 70 per cent. alcohol; acid v. 2.80; ester v. 0; sap. v. 2.80; ester v. after acetylation 35.47; free alcohol (calc. as $C_{10}H_{18}O$) 10.02 per cent.; phenols 8 per cent. *Iso*eugenol was proved to be present by its benzoyl derivative (m. p. 105°). Odour and boiling point (230°) rendered the presence of safrole very probable. In the distillation 90 per cent. of the oil passed between 170 and 230°, and 40 per cent. between 170 and 210°. The latter fraction had an optical rotation of $\alpha - 6^\circ 10'$ and a pronounced smell of cineole. The oil was decomposed at 240° (according to A. Müller[3]) an oil of a deep indigo-blue colour passed between 255 and 256°). By means of petrol ether about 0.23 per cent. of a brown oil of the following constants:— d_{15° 1.0237; $\alpha_D - 9^\circ 28'$; acid v. 9.33; ester v. 0; sap. v. 9.33; was obtained from the aqueous distillate.

Pimento Leaf Oil.—Very little is at present known concerning the properties of pimento leaf oil. We therefore reproduce the constants of two oils of guaranteed purity coming from Jamaica:—

	d_{15°	α_D	n_{D20°	eugenol	solubility in 70 per cent. alcohol
I.	1.0638	$\pm 0^\circ$	1.53897	96 per cent.	1 vol. and more
II.	1.0646	$-0^\circ 8'$	1.53963	96 per cent.	1 vol. and more

The oils were of a yellowish-brown colour and resembled clove oil in their odour.

Pine Leaf Oils.—The following two chief species of Douglas firs, frequently designated by the same name *Pseudotsuga Douglasii,* Carrière, should, according to A. Henry and M. G. Flood[4]), be differentiated.

(1) The Oregon Douglas fir (green fir?, red fir), *Pseudotsuga Douglasii,* Carrière, growing on the west coast of America; (2) the Colorado Douglas fir (blue fir), *pseudotsuga glauca,* Mayr., a native of the Rocky Mountains. The Oregon species is distinguished by its beautiful, stately trees which are valuable in many respects and hence cultivated in other countries:—They have, for instance, been planted in the good, deep-sandy soil

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[1]) Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. II, p. 487. — [2]) *Bull. Roure-Bertrand Fils,* April 1920, 35. — [3]) *loc. cit.* — [4]) *Perfum. Record* **11** (1920), 218.

of Highfield, East Liss, Hants, and in the Bagley Forest, near Oxford, where they have been yielding large bulks of timber in the short time, of 50 to 60 years. The Colorado Douglas fir is smaller and less useful as timber.

Apart from these two species Henry and Flood distinguish and characterise five other Douglas firs by the different textures of their leaves. The leaf of the Colorado fir, *e. g.*, showed the peculiar xerophytic features and was therefore adaptable to the dry continental climate of the Rocky Mountains. The odour of the needles (leaves) changes with the variety of the tree; whilst the Oregon tree has the pleasant smell of fir cones, the Colorado species has a rather sharp odour reminding of turpentine.

C. T. Bennett examined the leaf oils of the two species with the following results:—

(1) Leaf oil of *Pseudotsuga Douglasii,* Carrière, 50 lbs. of leaves of young trees from Avondale, England, gave in distillation less than 0.01 per cent. of a highly-aromatic essential oil which was not further studied. From older trees growing in Buckhold, Berks, England, 0.11 per cent. of an oil was prepared of the following properties:— d 0.876; α_D —7°; n_D 1.4835; ester (calculated as bornyl acetate) 12.4 per cent. The ester content was smaller than in the case of the Colorado oil, the odour was more fragrant. The oil contained *dipentene* and *limonene:* pinene was, if at all, present only in very small quantities since practically nothing distilled below 175°; of citral only traces were likewise present. The main constituent of the oil seems to be geraniol which was isolated by fractionation. Calculated as geraniol, the total alcohol contents amounted to 31.5 per cent. We should emphasise that geraniol had so far only been found in Australian callitris, but not in other oils of coniferae[1]).

(2) Leaf oil of *Pseudotsuga glauca,* Mayr. The leaves of medium-size trees from East Liss, Hants, England, yielded in distillation 0.31 per cent. of an essential oil with the following constants:—d 0.905; α_D — 46°; $n_{D20°}$ 1.4717; ester, calculated as bornyl acetate, 34.5 per cent. The terpenes consisted essentially of *pinene.*

Two investigations, by Brandel[2]) and Sweet and by Schorger[3]), had so far been published on Douglas fir leaf oils. When we compare their results with the researches of Bennett, we find that Brandel and Sweet were dealing with an oil of *Pseudotsuga Douglasii,* Carrière, and Schorger with a product resembling Colorado oil.

In this connection it should be mentioned that a striking analogy exists, as to the distribution and size of the fir cones and the different constitution of the oils, between the Douglas firs and the different species of "the yellow pines" of North West America. Thus the oil of turpentine from *Pinus ponderosa,* Laws.[4]), and *P. ponderosa var. caesia,* which grow in the same districts as the Oregon Douglas fir and have medium-size fir cones, contains essentially β-pinene; *Pinus ponderosa var. scopulorum,* Engelm.[4]), on the other hand, with small fir cones, and like the *Pinus glauca,* a native of the Rocky Mountains, gives an oil of turpentine consisting essentially of α-pinene. Finally from *Pinus Jeffreyi,* Murray, a tree characterised by very large cones and growing like *Pseudotsuga macrocarpa* in Southern California, we obtained an oil of turpentine containing 95 per cent. of heptane.

The *Oil of the Needles* of *Pinus montana,* Mill. ("Latschenkieferöl") (taken internally, 2 to 4 times daily, three drops, together with tincture of cinnamon, ether or the yolk of egg with brandy and sugar water) has been applied by M. Mayer[5]) with success in purulent and inflammatory troubles, especially with empyema after resection and with appendicitis.

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[1]) Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. II, p. 146. — [2]) Cf. *Report* April **1909,** 43. — [3]) *Report* April **1914,** 83. — [4]) Cf. *Report* April **1913,** 101. — [5]) *Münch. med. Wochenschr.* **1920,** 572. After *Therap. Halbmonatsh.* **34** (1920), 422.

Rose Oil, Anatolian.—An English report[1] on the oil of rose industry of Asia Minor expresses the opinion that the rose culture of Anatolia would be much older than that of Bulgaria. This statement may appear justified in so far as the rose cultivation and industry spread about the 17th century from Persia not only to the south, but also towards the north, into Asia Minor, Turkey and Bulgaria[2]. When we consider the statements of the Turkish geographer Hadji Chalfa[3], however, there were extensive rose fields in southern Bulgaria near Adrianople already in the first half of the 17th century, and the conclusion appears justified that this cultivation cannot for any long period have been restricted to Asia Minor. On the other hand G. Bredemann[5] asserts that the rose oil industry of Asia Minor was only founded in Anatolia by Turkish rose-peasants who had immigrated in the year 1894 from Bulgaria. We further regard the statement of the English report, that up till recently Anatolian rose oil had found its way westward under the designation of Bulgarian oil of rose, as very improbable. We are not acquainted with any evidence as to a rose culture existing in Asia Minor during the 18th and 19th century.

Since we reported at length a few years ago on a comprehensive paper by G. Bredemann[4] on "the oil of rose industry of Turkey and Asia", we need here only mention that P. Jeancard[5] has recently dealt with the same subject in an article which does not contain any new information.

Rose Oil, Bulgarian.—Reports coming from Bulgaria agree that we had correctly estimated the total yield of the harvest of 1920 in our last *Report* at 1100 kg. It is true that it is officially maintained, that this figure is too high, and that the last harvest had only yielded about 900 kg. It is certainly a fact that the yield has remained considerably below that of the year 1919. The price for pure oil is quoted at above 26000 levas, including a pure profit of 10 per cent., which would be equivalent to a price of about 22000 Mark in German money. The exports from Bulgaria are said to have amounted to not less than 2100 kg. in 1920. That would clearly show that there must still be a brisk trade with adulterated ware. Large bulks of all possible mixtures are said to be offered by smugglers in the producing districts. Within our own frontiers there also remained large stocks, partly objects of pledge, the examination of which makes the greatest caution advisable with respect to apparently-profitable offers.

The chances for 1921 are still more unfavourable. In consequence of gross neglect during the war, the plantations are reported to be in a simply-miserable condition and, though restoration is anxiously being pushed, it is still considered that at least 4 years will pass before a somewhat normal yield of flowers may again be expected.

Under these conditions we may again reckon upon a lively demand for our well-known and approved Miltitz rose products in the course of this year. We offer these in several nuances under the designations:—

Rose "Schimmel & Co." *(Red Rose)*
Rose "Schimmel & Co." *(Maréchal Niel)*
Rose "Schimmel & Co." *(Moss Rose)*
Rose "Schimmel & Co." *(Tea Rose)*
Rose "Schimmel & Co." *(White Rose).*

The basis for the preparation of these eminent floral oils is the extract which we prepare in our own plantations from the flowers of *Rosa damascena* and other sorts.

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[1] *Perfum. Record* 11 (1920), 210. — [2] Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 141. — [3] Cf. *Report* 1916, 47. — [4] Cf. *Report* 1917, 42. — [5] *Perfum. Record* 11 (1920), 210.

In view of the scarcity of the Bulgarian oil of rose we have in the last two years much expanded our plantations so that we hope to be able to satisfy a growing demand for our rose essences on a natural basis. We have at the present time 13.5 ha. under rose cultivation and, provided the weather be moderately-favourable within the next two months, we think we may rely upon a good harvest.

We may take this opportunity to draw attention also to our artificial rose oil.

On page 50 of our last *Report* we mentioned that the industry of oil of rose is no longer considered profitable in Bulgaria, and that consequently the cultivation of the roses is diminishing. Some exact figures as to the development and the present position of the industry in Bulgaria we take from a report of consul G. H. Kemper[1]) in Sophia.

According to this report the production of oil of rose in Bulgaria culminated during the years 1900 to 1912 when more than 20000 acres[2]) of roses were under cultivation yielding on an average about 126800 oz. of oil of rose. In this period a number of works were erected and equipped with modern distillation plants. During the three wars which Bulgaria carried on in the last decade, the production of oil of rose diminished more and more, and at present only 15000 acres are still supposed to be planted with roses. In each of the years 1917 and 1918, 85000 oz., and in 1919, 52000 oz. of rose oil were produced, and a further reduction is to be predicted for 1920. By the beginning of March 1920 some 50000 oz. of oil of rose of a value of 500000 dollars were stored in Bulgaria.

Rose Oil, French.—Up till the year 1911 the *Rosa damascena*, Mill., ("rose de mai") was, according to J. de Lorgues[3]), the only kind of rose which was cultivated in France for the perfume industry. At present, however, the oil is gained from "garden roses" which bear abundant flowers in spring[4]). Among these are to be counted:—Rose Brunner, Rose Vanhoutte, Paul Neyron, Souvenir de la Malmaison, Maréchal Niel, la France, Gloire Lyonnaise and Gabriel Luizet. As the cultivation of these garden roses is less expensive than that of the Rose de mai, the distillers are able to sell the products of the former at a reduced price. All these kinds of roses yield satisfactory results when the oils are extracted by means of solvents. On the other hand, the properties of the distilled oils vary much according to the nature of the flower and the mode of its treatment. The oil distilled from the Rose de mai had the following constants:—m. p. 25.5°; d 0.870 to 0.880; $\alpha - 3^\circ$; the oil of the Rose Nabonand:—m. p. 18°; d_{32° 0.8537; $\alpha - 2^\circ$; sap. v. 42; the oil of the Rose Vanhoutte:—m. p. frequently above 26°. A product prepared by Gattefossé from a mixture of these varieties:—m. p. 23 to 26°; d 0.862 to 0.867; n 1.4600 to 1.4638; geraniol 35 to 37 per cent.; citronellol 36 to 48 per cent.

Rose Oil, Indian.—Great exertions appear to be made in India to foster the decadent industry of oil of rose. In Siktara, a village near Hathras, manifold experiments have been made in this direction, on which we have a paper by J. P. Srivastava and D. N. Sinha[5]). At this place the *Rosa damascena* was cultivated, and it was found that they could easily reap 1200 lbs. of rose flowers per year per acre by contrast to the usual Indian crops of 500 to 600 lbs. per acre. The experiments further demonstrated

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[1]) *Americ. Journ. Pharm.* 92 (1920), 428. — [2]) 1 acre = 40 ares. — [3]) According to other reports *Rosa centifolia*, L., is the species which is chiefly utilised in Southern France for the manufacture of rose water and rose pomatum; cf. Gildemeister and Hoffmann, *The Volatile Oils*, vol. II., p. 552. — [4]) *Chemist and Druggist* 93 (1920), 1629. — [5]) *Perfum. Record* 12 (1921), 14.

that the yield of oil of rose could considerably be increased by protecting the suitable stills from the hot winds. The best results — a yield of 0.025 per cent. of oil of rose[1]) — were realised, when in a distillation carried on for a period of 3 hours the ratio of flowers to water was 1 : 4. The product contained 25 per cent. of steorophena (stearoptene is probably meant). According to the authors these results would justify the hope that Indian oil of rose might compete against the Bulgarian product. It might also be possible to breed a species richer in oil by careful cultivation; according to Parry roses of Persia and Cashmere had given from 0.05 to 0.066 per cent. of oil of rose. The authors has evidently overlooked that Parry[2]) queried this statement as uncertain. The few communications extant on Persian oil of rose do not give any yield figures. It is, on the other hand, certain that the rose of Shiras was distinguished by a very common scent and possessed also otherwise properties quite different from those of Bulgarian oil of rose[3]).

In Morocco roses suitable for the preparation of oil occur only near Marrakesh and near Fez. There are about 10 undertakers in this line in Marrakesh, and they consume per month 10000 kg. of dry leaf flowers which yield 5500 kg. of rose water. A good many of the middle-class inhabitants of the country also distil their own rose water[4]).

An oil of rose which was offered to us for purchase was as badly as clumsily adulterated, as the following constants show:—d_{30° 0.8610; α_D —0°8′; n_{D25° 1.44471; solidification point 18.8°; acid v. 1.4; ester v. 172.2; ester v. after acetyl. 193.1.

Apart from the too-small refraction (normal 1.452 to 1.464) and the too-low acetylation value (normal 203 to 228); the ester value must above everything be considered far too high; for the ester value of pure oil of rose ranges only from 7 to 16. This discrepancy would alone suffice to mark the sample as adulterated; cocos oil seemed to have been used. As the saponification value of this oil is 260, the analysis would indicate an addition of 60 per cent. of this oil! Another adulteration should also be taken into consideration; for the presence of the cocos fat would not account for the low acetylation value of the oil. We did not enter upon the detailed examination of this oil owing to its high price; the recognition of the gross adulteration was quite sufficient to make us reject the oil.

We will assume in favour of the seller that he had no idea of the peculiar character of this oil; otherwise we should have to consider it very naive that he should offer us such a product.

Rosemary Oil.—As regards Spanish rosemary oil, see page 80 of this *Report*.

Rue Oil.—As regards Spanish rue oil, see page 77 of this *Report*.

Sage Oil.—As regards Spanish sage oils, cf. page 79 of this *Report*.

Sandalwood Oil, West Australian.—In our last *Report*[5]) we reproduced some communications on the mother plant and the occurrence of sandalwood oil from West Australia. As there are no statements available concerning the chemical con-

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[1]) We obtained about 0.016 to 0.02 per cent. of oil from *Rosa damascena*. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 560. — [2]) *The chemistry of essential oils and artificial perfumes*, 1899, p. 290. — [3]) Cf. *Report* October 1897, 49; April 1914, 87. — [4]) *Rev. des produits chim.* 22 (1919), 647. — [5]) *Report* 1920, 54.

stitution of this oil, and as it has been suggested by one journal[1]) that there may be one or several isomerides of santalol in the alcoholic constituents, we have been attempting to clear up the question whether santalol or the sesquiterpene alcohols related to this compound really form the essential constituents of this oil. We had a large bulk of material from a reliable source in London at our disposal for this examination, namely 600 g. of a material of the following constants:— d_{15° 0.9720; $[\alpha]_D + 4^\circ 9'$; n_{D20° 1.50900; insoluble in 10 vol. 70 per cent. alcohol, soluble in 1.5 vol. and more 80 per cent. alcohol; acid v. 1.5; ester v. 16.2 = 6.4 per cent. estersantalol; ester v. after acetylation 165.2 = 74.1 per cent. total santalol.

The oil was by twofold fractionation separated into the following fractions:—

1. b. p. (70 to) 100 to 135° (6 mm.) 135 g.
2. „ 135 „ 145° „ 56 g.
3. „ 145 „ 150° „ 92 g. (d_{15° 0.9851; $[\alpha]_D + 4^\circ 26'$)
4. „ 150 „ 153° „ 116 g. (d_{15° 0.9824; $[\alpha]_D + 7^\circ 18'$)
5. „ 153 „ 160° „ 141 g. (d_{15° 0.9825; $[\alpha]_D + 7^\circ 52'$)
6. „ 160 „ 182° „ 27 g.
7. „ residue 10 g.

The fractions 2 to 5 all possessed a faint odour like mint with a more or less distinct suggestion of santalol. We were, however, not able to convert one of these alcoholic fractions into the phthalic ester by the usual method (heating for one hour of the benzene solution with phthalic acid anhydride on the water bath). We also failed to esterify the fractions boiling between 145 and 150° (6 mm.) with benzoylchloride and pyridine and likewise the subsequent fraction 4 (as sodium compound) in petrol ether with phthalic acid anhydride. On the other hand we obtained from the last-mentioned fraction, by boiling with acetic acid anhydride on the sand bath, easily the acetate:—b. p. 156 to 158° (5 mm.), sap. v. 216.2 = appr. 100 per cent. $C_{15}H_{23}O \cdot CO \cdot CH_3$, which in its odour bore a strong resemblance to the acetic ester of santalol. The phthalic ester, however, was prepared from the fractions mentioned by heating for four or six hours on an oil bath, and in one case, at the end of this research, by heating for the same period on a water bath at 80°. About 50 per cent. of these fractions did not take part in the reaction. A solid phthalic ester acid was not obtained. The alcohol fractions which the saponification of the esters yielded had the following constants[2]):—

Fraction 5 (ca. 140°, 6 hours). d_{15° 0.9898; $[\alpha]_D + 9^\circ 16'$; n_{D20° 1.51470; b. p. 146 to 149° (4 to 5 mm.);

fraction 3 (ca. 135°, 3 to 4 hours). d_{15° 0.9843; $[\alpha]_D - 3^\circ 18'$; n_{D20° 1.51184; b. p. 149 to 152 (6 mm);

fraction 4 (ca. 80°, 3 hours). d_{15° 0.9767; $[\alpha]_D + 6^\circ 18'$; b. p. 141 to 143° (3 to 4 mm.).

All the preparations had a faint odour of santalol and did not react with phenyl- and α-naphthyl-*iso*cyanate, in analogy to santalol. The results of a combustion test of the preparation from fraction 3 agreed with the formula $C_{15}H_{24}O$:—

(1) 0.2369 g. of substance: 0.7092 g. CO_2, 0.2306 g. H_2O; found C 81.65 p.c., H 10.81 p.c.
(2) 0.2112 g. of substance: 0.6344 g. CO_2, 0.2068 g. H_2O; found C 81.81 p.c., H 10.88 p.c.
Calculated for $C_{15}H_{24}O$: 81.82 p. c. C., 10.91 p. c. H.

When formic acid was added to the alcohol, water was split off on heating.

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[1]) *Americ. Perfumer* 15 (1920), 284. — [2]) We add for comparison the constants of santalol from East Indian oil:— d_{15° 0.9761; $[\alpha]_D - 17^\circ 44'$; n_{D20° 1.50790; b. p. 138 to 140° (4 mm.).

These statements seem to justify the conclusion that the alcoholic fractions of the oil from West Australia contain a mixture of one or several sesquiterpene alcohols, essentially not reacting with phthalic acid anhydride, and of santalol or of an alcohol very similar to it. The result of the following oxidation tests would confirm the identity of this alcohol with santalol.

According to Semmler[1]), santalal (wich is obtained from santalol by oxidation with chromic acid anhydride in glacial acetic acid) of a boiling point of 152 to 155° (10 mm.) yields a semicarbazone of a melting point of about 230°. In the repeated preparation of santalal from santalol from East Indian oil we obtained on the contrary semicarbazone which melted between 215 and 219°; semicarbazones of the same melting point were also obtained in repeated experiments with alcohols (from West Australian oil) esterified with phthalic acid anhydride by means of chromic acid and glacial acetic acid. Depressions of the melting point amounting to more than 1° were never observed in mixtures of the semicarbazones from santalol and the aldehyde (from esterified alcohol of West Australian oil).

Attempts to prove the presence of *betulol* by the preparation of tri*cyclo*betulol according to the method of Semmler[2]) failed, both in the esterified and in the alcohol preparations of West Australian oils of corresponding boiling point which did not react with phthalic acid anhydride.

From the fractions 1 and 2 we isolated by repeated fractionation a sesquiterpene (65 g.) of b. p. 106 to 110° (3 to 4 mm.), d_{15° 0.9157; $[\alpha]_D - 2° 15'$; n_{D20° 1.49968; this fraction reacted only weakly with sodium on boiling. The solution in ether, saturated with hydrogen chloride and strongly cooled, deposited after standing and evaporation of the ether, scaly crystals which, recrystallised from methyl alcohol, melted between 79.5 and 80.5°.

The analysis showed that these crystals represent a *trihydrochloride*, evidently identical with that of *bisabolene*.

0.1822 g. of the substance gave 0.2487 g. AgCl.

Chlorine found 33.76 per cent. Calculated as $C_{15}H_{24}(HCl)_3$ 33.97 per cent.

Considering the small amount of this sesquiterpene-derivative its contents of this oil can only amount to a few per cent. We, therefore, did not attempt in this investigation to ascertain whether the oil really contains bisabolene as such, or a sesquiterpene which passes into a derivative when treated with gaseous hydrochloric acid. Since bisabolene is an aliphatic sesquiterpene of specific gravity 0.8759, we should have to assume in our case that our sesquiterpene fraction was highly contaminated with some other sesquiterpene hydrocarbon of the same boiling point.

We add here the results of tests of West Australian sandalwood oil conducted in the Imperial Institute of London[3]). The constants determined were: — d_{15° 0.958; $[\alpha]_D - 0° 25'$; n_D 1.503; acid v. 2.9; ester v. 4.7; after acetylation 170.8; total alcohol ($C_{15}H_{24}O$) 76.3 per cent.; insoluble in alcohol of 70 per cent. By oxidation with permanganate 8 per cent. of santalenic acid were obtained; an East Indian oil with 95 per cent. of santalol gave 24 per cent. of santalenic acid. These results likewise indicate that small quantities of santalol were present in addition to other alcohols.

In another journal[4]) it is mentioned that sandalwood can be found in West Australia on a area twice as large as Great Britain, and in small quantities also in Victoria, New South Wales, and Queensland. It becomes more difficult, however, from year

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[1]) *Berl. Berichte* **40** (1907), 1126. — [2]) *Ibidem* **51** (1918), 420. — [3]) *Bull. Imp. Inst.* **18** (1920), 162. — [4]) *Chemist and Druggist* **93** (1920), 1228.

to year to gather the wood; yet the manufacture of the oil has been resumed in the hope that the British Pharmacopœia will recognise the product which could then find medicinal use outside Australia.

Savin Oil.—It has been pointed out from various sides some years ago already[1]) that the oil of *Juniperus phœnicea* is frequently offered in the south of France as genuine sabine bush oil (from *Juniperus sabina*, L.). Owing to the great resemblance between the two shrubs, this is probably ignorance rather than fraudulent intent. The same thing seems to occur in Spain; at any rate we were offered last year several sabine bush oils from Spain which in reality had nothing to do with this particular oil and which to all appearance had been distilled from *Juniperus phœnicea*, as the following comparative table will render clear:—

	Sample			Oil of *Juniperus phœnicea* observed by		Savin oil
	I	II	III	Rodié and by Schimmel & Co.	Umney and Bennett	
d_{15° . . .	0.8681	0.8800	0.8822	0.863 to 0.872	0.892	0.907 to 0.930
α_D	$+1^\circ 54'$	$+1^\circ 47'$	$+0^\circ 45'$	$+2^\circ$ to $+7^\circ 20'$	$+4^\circ 30'$	$+38^\circ$ to $+62^\circ$
Acid v. . .	0.3	0.6	1.2	—	—	up to 3
Ester v. . .	8.4	14.5	18.7	0 to 2.1	26	101 to 138
Acid v. after acetylation	9.3	42.5	—	4.7 to 11	60	127 to 154
Solubility in 90 per. cent. alcohol	6 vol. and more	3 vol. and more	4 vol. and more	5 to 6.5 vol. and more	—	0.5 vol. and more

Oil I. was said to have been prepared from the *fruit*. We are rather inclined to doubt that and believe that we had in all the three cases to deal with the distillate from the tips of the *twigs* of *Juniperus phœnicea*. We should add that the oils indicated a constitution different from sabine bush oil also by their scent; in this respect they resembled oil of turpentine and oil of juniper berries to a certain extent.

What we have said will make it advisable to be cautions in buying Spanish, as well as French savin oils.

As regards Spanish savin oils, see page 75 of this *Report*.

Oil from the Fruit of Selinum Monnieri.—From the fruit of *Selinum Monnieri*, L., an umbellifera which grows in China under the name of *she-chuang-tzu* and which is used as aphrodisiac and sedative, Manzo Nakao[2]) obtained by steam distillation 1.3 per cent. of a light yellow essential oil, smelling of oil of turpentine and of the following constants:—d_{15° 0.896; $[\alpha]_D - 42.7^\circ$; acid v. 1.63, sap. v. 23.62, sap. v. after acetyl. 51.35. Three fractions of the oil were separated:—154 to 157°, ($[\alpha]_D - 55.42^\circ$, containing l-*pinene* as proved by the hydrochloride and nitrosylchloride)[3]); 157 to 160°, ($[\alpha]_D - 53.4^\circ$, containing *camphene*)[4]); and 200 to 250°, ($[\alpha]_D - 33.14^\circ$, containing an ester [sap. v. 229] consisting of l-*borneol* and iso*valeric acid*); phellandrene, cineole and terpineol could not be found.

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[1]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 175. *Report* April **1906**, 61; April **1907**, 93. — [2]) *Yakugakuzasshi* **462** (1920); from *Journ. de Pharm. et Chim.* VII. **23** (1921), 141. — [3]) The constants of these compounds are not stated. — [4]) It is not stated how camphene was identified.

Sheih Oil.—By the name of *Sheih* or *Chieh* the Arabs designate plants of strong odour growing in North Africa, the essential oils of which have been investigated by E. Grimal1), P. Jeancard and C. Satie2) and by Schimmel & Co.3). Grimal states that he obtained the oil from the *Artemisia herba-alba,* Asso, which is common in Algiers; Jeancard and Satie do not give any further information as to their plant which also came from Algiers; Schimmel & Co. had experimented with the *Artemisia herba-alba* var. *densiflora,* Boiss.

Roure-Bertrand Fils4) have recently further investigated a sheih oil from Algiers. In the course of this investigation E. G. and A. Camus found that *Artemisia herba-alba* occurs in North Africa in four different varieties:—(1) var. *genuina*, Battand et Trab., widely distributed; (2) var. *patula*, Battand et Trab., also commonly found; (3) var. *oranensis,* Debeaux Assoc. (fr. Congrès d'Oran, Oran); (4) var. *densiflora*, Boissier, Sahara.

The oil examined by Roure-Bertrand Fils came from *Artemisia herba-alba,* Asso var. *genuina,* Battand et Trab. Since this plant, sometimes also called white mugwort, grows in ample quantities in Algiers, but only in the high mountains, it was not quite easy to obtain the necessary material. The same authenticated sample of this scheih oil was studied before and after the war. It was then ascertained that the oil had strongly changed during the six years of storage, and that resin acids had been formed in particular at the expense of the free alcohols. Especially noteworthy was, in addition to the large increase in the acid value (from 3.5 to 29.87) and to the diminished solubility in alcohol, the change in the optical rotation (from $+2^\circ 6'$ to $-13^\circ 24'$). The constants of the two samples were the following:—

Date of examination.	1914.	1920.
colour	light brown	brown
d_{15°	0.9432	0.9534
α_{D17°	$+2^\circ 6'$	$-13^\circ 24'$
solubility in 70 per cent. alcohol	in 1.4 vol. (turbidity)	almost insoluble
acid v.	3.5	29.87
ester v.	53.9	53.2
ester v. after acetyl.	147	84
total alcohol (calculated as $C_{10}H_{18}O$)	45.44 per cent.	24.65 per cent.
free alcohol	30.64 per cent.	10.01 per cent.

After a second steam distillation the stored oil yielded 72 per cent. of an almost colourless liquid, the odour of which suggested cineole, menthol and camphor; the properties were:—d_{15° 0.9365; α_{D15° -19°; n_{D15° 1.4710; soluble in 15 vol. of 60 per cent. alcohol, in 1 vol. of 70 per cent. alcohol, easily soluble in 80 per cent. alcohol; acid v. 7.47, ester v. 41,06, sap. v. 48.53; ester v. after acetyl. 41.06; total alcohol (calculated as $C_{10}H_{18}O$) 11.29 per cent.; free alcohol 0 per cent. The distillation residue (about 25 per cent. of the original oil) was a sluggish liquid, deep red brown, of balsamic odour and the following constants:—d_{16° 0.9685, acid v. 93.33, ester v. 82.13, sap. v. 175.46; ester v. after acetyl. 163; total alcohol (as $C_{10}H_{18}O$) 46.26 per cent.; free alcohol 23.68 per cent. The new distillate was distilled in *vacuo* and gave the fractions:—60 to 105° (25 mm.) 7.0 g., $d_{16^\circ}^{16^\circ}$ 0.9065, α_{D16° $-27^\circ 36'$; 105 to 110° (25 mm.) 9 g., $d_{16^\circ}^{16^\circ}$ 0.9469, α_{D16° $-32^\circ 4'$; 110 to 120° (25 mm.) 6 g., $d_{16^\circ}^{16^\circ}$ 0.9531, α_{D16° -39°; 120 to 125° (14 mm.) 3 g., $d_{16^\circ}^{16^\circ}$ 0.9563, α_{D16° $-31^\circ 12'$; 125 to 130° (14 mm.), 1.5 g., α_{D16° $-7^\circ 40'$; residue 2 g.

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1) Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. III, p. 648. — 2) *Ibidem,* p. 668. — 3) *Ibidem,* p. 649. — 4) *Bull. Roure-Bertrand Fils,* avril 1920, 18.

Contrary to Grimal they could not find any dextrorotatory fraction. On the other hand they ascertained the presence of *l*-camphene, cineole and *l*-camphor, in accordance with Grimal. The freshly-distilled oil contained in addition 25.26 per cent. of ester, calculated as $CH_3CO_2C_{10}H_{17}$, 30.64 per cent. of free alcohols, calculated as $C_{10}H_{18}O$, and probably menthol.

Oil of Skimmia Laureola.—A sample of an essential oil[1]) from *Skimmia laureola*, Hook. f. had, according to Roure-Bertrand Fils[2]), the following properties:—d_{18° 0.8931; α_{D18° $+4^\circ 28'$; acid v. 0; sap. v. 82.13; soluble in three volumes of 90 per cent. alcohol becoming turbid with more alcohol. The oil was light-green and smelled strongly of laurel oil and a little of polei oil.

Skimmia laureola (Rutaceæ), also known under the name *limonia*, is an evergreen shrub of strong odour, up to 1.5 m. in height, which grows in India and Afghanistan in the mountains at altitudes from 1500 to 3000 m. The bruised leaves exhale a strong odour of oranges, and they are used in India both as a medicine and a spice and incense. The soft wood of the plant is likewise of an aromatic smell.

Star Anise Oil.—After continuous decline the marked has finally come to a low level which is unprecendented in the history of this important article. If a price of 3 s. per lb. was extraordinarily low even before the war, prices have been going down to 2/1 d. within the last weeks. Although that was partly due to baisse speculators, extensive business has yet been done. The further development of the prices will in the first instance depend upon the condition of the Chinese silver valuta.

Thyme Oil.—E. M. Holmes[3]) contributes a further paper on Spanish thyme oil which is partly based upon the work of Parry and of Dorronsoro (confer page 81 of this *Report*). There are in Spain not less than 30 different species of thyme, which are enumerated in the *Compendio de la Flora Española* published by Blas Lazaro e Ibiza in the year 1907, and at least two more species have been described since this publication. From the fact that at least nine of these thirty-two species are known by popular names, we may conclude that these nine species are of common occurrence and that they will find manifold applications in the country. The Spanish thyme oil, which used to be introduced into England in former years, contained more phenols (50 to 70 per cent., chiefly carvacrol) than the French product. The author and H. Rubeck observed later that of the Spanish species *Thymus zygis*, L. and *T. vulgaris* (both called *tomillo salsero* in the country) contained considerable quantities of thymol.

In order to determine the thymol contents in Spanish thyme oils H. Mastbaum[4]) extracts the phenols from the oil by means of 5 per cent. caustic soda and precipitates them from the alkaline solution by acidulation. The carvacrol which remains liquid is drained off from the crystallising thymol. The thymol contents is deduced from the weight of the thymol crystals after pressing and drying. The thymol weighed not being quite pure, whilst a little thymol remains in the carvacrol, Mastbaum supposes that the one source of error would balance the other, and that the final result would be sufficiently accurate for practical purposes. Whether or not the amount of thymol which remains dissolved in the carvacrol is really of no consequence for the total results of the analysis will probably have to be settled by further experiments. In our

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[1]) It is not mentioned from which parts of the plant the oil was obtained. — [2]) *Bull. Roure-Bertrand Fils*, October **1920**, 34. — [3]) *Perfum. Record.* **11** (1920), 338. — [4]) *Chem. Ztg.* **45** (1921), 19.

own experience the thymol can never quantitatively be separated by the method of Mastbaum from mixtures of these phenols, unless the percentage of carvacrol should happen to be very low.

As regards Spanish thyme oils see page 81 of this *Report.*

Turpentine Oil.—According to E. S. Oliver[1]) British Columbia may have a future as a country for producing turpentine, provided that the gathering of the turpentine be no longer conducted in the old imperfect way, but according to an improved method of his own.

Oliver reports that the first ship which was sent from England to the American coast carried a letter written by Queen Elizabeth's own hand giving instructions as to the way of gathering tree resins. Applying this old method—the bark is cut and the resin collected after the volatile constituents have been oxidised by contact with the air—they had so far not been able to obtain more than 17$^1/_2$ per cent. of the possible yield of turpentine. Oliver recommends merely to bore a small hole into the trunk and to apply a bottle close to the hole. In this way he would gain at least 33 per cent. of the turpentine. The tree would, moreover, not only be spared, but its growth would even be stimulated[2]).

As regards the formation of resin Oliver has proposed a peculiar theory which we will outline. According to this theory most pine trees have survived the cold period which covered the northern hemisphere many years ago. The trees were only enabled to survive this cold age by secreting a non-freezing substance such as turpentine which surrounded and protected the cells. When the climate became warmer once more, the turpentine had lost its proper and original significance (according to Oliver) and formed merely a superflous assimilation-product, of which the tree wanted to get rid again as quickly as possible.

The resins obtained from Douglas firs in Columbia are utilised in manifold ways, for instance, for the preparation of fine varnishes, of printers' ink and of snow-white Burgundy pitch. The colour varies with the quality of the resin, from deep-red to light-green and milky-white. The light-green is considered the finest kind.

On Cortez Island, at the mouth of the Campbell River, some 60 English miles from Vancouver, a small company has already started on the utilisation of resin. It is estimated that 100 acres of Douglas firs will there give yearly about 800 lbs. of resin.

With respect to the French industry of turpentine during the last years the *Industrie- und Handelszeitung*[3]) makes the following statements, based on English information. There were obtained in the forest of Gascogne near Bordeaux:—

	1913	1914	1915	1916	1917	1918	1919	1920 (estimated)
Colophony[4]) . .	85000	64000	43000	60000	60000	68000	85000	120000 tons.
Oil of turpentine	25000	19000	12000	17000	17000	20000	25000	35000 „

It is believed that the main portion of the last harvest will be exported and will yield 180000000 fr., that is, twice as much as in the year 1919. A decree of October 23, 1920, forbade the exports of oil of turpentine without special license[4]); where a license is granted, an export duty of 20 per cent. will be exacted. Semi-

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[1]) *Chem. and met. Eng.* **23** (1920), 238. — [2]) See Wislicenus, *Bericht* (Germ. ed.) **1918**, 53. — [3]) *Oil and Colour Trades Journ.* From *Ind. u. Handelszeitung* No. 40, Feb. 17, **1921**, supplement. — [4]) The paper speaks always of turpentine and resin; the English word turpentine (= turpentine or oil of turpentine) has evidently been translated *Terpentin,* instead *Terpentinöl.* Oil of turpentine and colophony are meant.

officially it was announced that this prohibition of exports of oil of turpentine would be postponed till March 1921. The prices generally went down in Bordeaux and Dax. In the Landes the quotations were:—oil of turpentine 550 fr. per 100 kg. f. o. r., colophony 160 fr. each per 100 kg. under the same conditions.

In a turpentine from Wen-Chou (China) Y. Shinosaki and Ono¹) found 84.35 per cent. of resin and 8.15 per cent. of an essential oil of the following constants:—d_{15° 0.8670; $[\alpha]_D - 31.41^\circ$; n_{D20° 1.4711; soluble in 8.8 vol. 90 per cent. and in 28.8 vol. 80 per cent. alcohol. The oil contained 85 per cent. of α-pinene, traces of dipentene and 11 per cent. of a new tricyclic sesquiterpene $C_{15}H_{24}$ (b. p. 92 to 93° [2.5 mm.]; d_{15° 0.9408; d_{20° 0.9398; $[\alpha]_D + 47.31^\circ$ [in ether]; n_{D20° 1.5031). This last body was isolated as monohydrochloride (m. p. 58 to 59°) by passing hydrochloric acid gas into the ethereal solution of the fraction distilling between 90 and 105° (2.5 mm.).

According to English news²) there is a great demand for oil of turpentine in India³). On the other hand colophony is little required, and great stores of this material are accumulating. For this reason the "Rosin and Turpentine" works in Jallo have experimentally been producing from turpentine, by dry distillation, resin gas, resin spirit, resin oils and pitch. The yield and quality of the products being satisfactory and the purification not too elaborate, it is hoped that the large-scale manufacture will be started in a few months.

The English article quoted mentions in this connection that the American "Naval Stores"⁴) had to pass through a similar phase in their early days. There was only use for the oil of turpentine originally; the rosin remaining in the distillation was thrown into the river or into holes dug into the earth. Those spots were afterwards known as „rosin mines". When later on colophony began to become valuable, many people gained a subsistence by fishing the rosin up again and selling it.

The chemical laboratory of the United States Dept. of Agriculture⁵) describes the following simple tests, by means of which, with a little practice, *adulterations* of 10 per cent. and more could easily be recognised in oil of turpentine. Kerosene, gasoline, benzene, solvent naphtha are recognisable by their odours. Oil from wood-turpentine (American *Kienöl,* pine wood oil) is easily distinguishible from turpentine by its smell. If a sample leaves a grease spot on white paper, it will probably be adulterated with kerosene or with a heavy solvent naphtha. A good deal of heavy oil of turpentine, boiling above 170°, may also be present. When a small bottle, quite clean and dry, is half filled with oil of turpentine and shaken for an instant, the foam first appearing will vanish at once again, if the oil be pure and fresh. When the foam persists for more than 5 seconds, the oil must be suspected of being adulterated or old. By the following method of evaporation any mineral oils can also be recognised:—Pour 5 cc. of the oil of turpentine upon a large watch glass and take up 2 cc. of this oil again by means of a pipette. When after 3 hours the margin of the fine film of oil looks homogeneous and regular, the sample was pure. Any drops, froth or striæ suggest adulteration.

Starting from the work of Armstrong⁶), who made the first investigation of the adulteration of oil of turpentine, H. Salvaterra⁷) reviews the abundant methods of the

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¹) *Journ. chem. Ind.,* Tokyo **23** (1920), 45. From *Chem. Abstracts* **14** (1920), 2928. — ²) *Chemist and Druggist* **93** (1920), 1345. — ³) Cf. *Report* **1920**, 127. — ⁴) Cf. *Report* **1916**, 56 and Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. I, p. 94. — ⁵) *Americ. Journ. Pharm.* **92** (1920), 931. — ⁶) *Journ. chem. Soc.* **52** (1882), 478. — ⁷) *Chem. Ztg.* **45** (1921), 133, 150, 158.

literature on the examination of oil of turpentine. His own experiments lead the author to the conclusion that the oxidation method with mercury acetate according to Tausz¹), the bromination method according to Allina-Salvaterra²), and the iodine-addition method as modified by the author will answer their purpose and will mutually supplement one another. With pine tar oil, about 10 per cent. will separate from the steam distillate by the mercury acetate method. Since such a separation does not occur with the other methods, any addition of that oil can be discovered by multiplying the difference obtained in the separations according to Tausz and to Allina-Salvaterra by 10. In the presence ot tetrahydronaphthalene this pine tar oil determination is not possible, since tetralin reacts partly with the halogen.

A. Allina and H. Salvaterra³) have also published an extensive research on the *determination of light petroleum* in oil of turpentine. The methods of H. Herzfeld and J. Marcusson⁴), so far applied for this determination in oil of turpentine and in pine tar oils, are based upon a violent destruction of the terpene hydrocarbons and do not always give satisfactory results. The method recommended by Allina and Salvaterra renders it possible to separate oil of turpentine and light petroleum and to determine the light petroleum contents without any destructive reaction. According to this method the physical properties of the sample are so altered by the bromination of the oil that only the non-brominated light petroleum will pass over in the steam distillation and can then easily be determined.

The authors recommend a few preliminary tests which are based upon the following observations:—(1) rise of temperature of the sample on addition of sulphuric acid of the concentration 2:1 (2 + 1?); (2) determination of the expansion coefficient; (3) increase in the specific gravity by the bromination; (4) determination of the quantity of bromine taken up, by means of the weight of hydrogen bromide required for the bromination.

These preliminary tests do not, it is true, admit of an exact determination of the petrolether percentage, but they are valuable for the recognition of the adulterations and also for the rapid distinction between oil of turpentine and so-called patent oil of turpentine, such as the Customs Authorities require, or for the distinction between oil of turpentine and pine tar oil.

In the bromination of oil of turpentine no analytical value must be attached to the absolute quantity of the bromine consumed even when the analyses are performed under constant conditions, because the reactions may be extremely complex and involve addition and substitution and breaking-up of the ring.

On the other hand it is a valuable fact that the boiling points of all the terpenes are raised by the bromination so that a separation of the light petroleum by distillation becomes easily possible. The bromination is best effected by bromine *in statu nascendi*, by the decomposition of bromic acid by means of hydrogen bromide. In this reaction pine tar oils and oils of turpentine do not behave in the same way, because the attack by bromine of the pine tar oil is much more sluggish than in the case of the oil of turpentine. Bromination by hypobromous acid does not offer any advantage over the just described method.

As regards the determination of oil of turpentine in the oil of the Siberian fir, J. W. Howorth⁵) describes a method, according to which he recognises adulteration by the oxidation of oil by means of air under addition of $\frac{N}{10}$ potassium iodide solution

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¹) *Chem. Ztg.* **42** (1918), 349. — ²) See next reference. — ³) *Chem. Ztg.* **44** (1920), 673 and 697. — ⁴) Cf. *Report* April **1910**, 114. — ⁵) *Pharmaceutical Journ.* **104** (1920), 345.

and titration of the iodine liberated. A control test with unadulterated oil is performed at the same time. According to the author the method is based upon the determination of the pinene contents of the sample. We should say that this purely-empirical method can never give reliable values and should be regarded with caution.

According to Lodemann¹) symptoms of real *poisoning by oil of turpentine* were observed in one case. The patient swallowed by mistake a large draught of oil of turpentine in the morning; he complained first of headaches; by noon he suffered from drowsiness and dizziness and fell into a state of heavy intoxication; convulsions and pains in the rectum followed in the next two nights, and the complete restoration of the patient required 8 days.

As regards Spanish oil of turpentine see page 74 of this *Report.*

Vetiver Oil.—As regards vetiver oil from the Philippines see page 85 of this *Report.*

Wintergreen Oil.—Wintergreen oil, sweet birch oil or synthetic methylsalicylate can, according to Power²), be identified in the following way:—Pour 1 cc. of the oil under test with 10 cc. of caustic soda of 5 per cent. into a test tube³). When the mixture is shaken a massive white crystalline precipitate will appear and will vanish again when the test tube, loosely corked, is held for five minutes in boiling water. We then obtain a clear, colourless or faintly-yellow solution in which there should not be any separation of oily drops, neither on the surface, nor on the bottom of the test tube. That observation proves the absence of other essential oils or of petroleum. When the liquid is diluted with the threefold bulk of water and a slight excess of hydrochloric acid is added, a white crystalline precipitate will form which, collected on a filter, washed with a little water and recrystallised from hot water, will give the reactions characteristic of salicylic acid (absence of methyl benzoate, &c.).

Ch. H. La Wall⁴) reviews the identity-reactions of the literature on *methyl salicylate, gaultheria* and *Sweet Birch oil.* Whilst methyl salicylate, being a synthetic product, comes into the trade in a high state of purity, the gaultheria oil contains up to 99 per cent. of this ester and in the rest a paraffin, an aldehyde, a ketone⁵), an alcohol and an ester. Sweet birch oil consists of up to 99.5 per cent. of methyl salicylate and, in the rest, of a paraffin and an ester, but contains neither alcohol nor aldehyde. These slight differences are decisive for a few colour reactions, by means of which unmixed products may be distinguished from one another under certain conditions. This is, for instance, possible by means of the test of Umney⁶), and also by means of a reaction, quoted by the author, which is based upon the determination of furfuraldehyde by means of aniline acetate:—Gaultheria oil is at once coloured an intense red by means of aniline acetate; sweet birch oil gives a pronounced reddish colour only after some time, and methyl salicylate remains colourless. If we have to deal with mixtures, on the other hand, it will be impossible to arrive at any reliable results by means of these colour reactions. The methods proposed by Stanislaus and Semmel (1913) and by Watson and Sayre (1914), which are based upon the colours produced by nitric acid, sulphuric

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¹) *Med. Klinik* **1920**, No. 13. *Pharm. Ztg.* **65** (1920), 511. — ²) *The Western Druggist,* Febr. **1917**; from *Deutsche Parf. Ztg.* 6 (1920), 208. — ³) On former occasions Power and Kleber had used caustic potash which forms a readily soluble ester salt with the ethyl salicylate; see *Pharm. Rundschau* (New York) **13** (1895), 228. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. III, p. 388. — ⁴) *Amer. Journ. Pharm.* **92** (1920), 891. — ⁵) According to Power and Kleber gaultheria oil contains either an aldehyde **or** a ketone. Cf. Gildemeister and Hoffmann, *loc. cit.* vol. III, p. 389. ⁶) Cf. *Report* April **1914**, 98.

acid and formaldehyde or merely by sulphuric acid, the author himself considers entirely unreliable, thereby confirming the opinion which we expressed at that time concerning the value of these reactions[1]).

Wormseed Oil, American.—The prices in the United States have continuously been receding during the last months, much to the advantage of the many producers of vermifuges. Although our New York friends supply us regularly with larger quantities, the supplies had not always come up to the demand. We have now, however, been able to take mesures which will prevent any further inability on our part to meet the demands. We should on this occasion once more emphasise that the greatest possible caution should be exercised in the purchase of this oil, because it is applied internally. Cheap wormseed oils are still being advertised in the newspapers, which carry their name without right and the use of which for medicinal purposes might cause the respective manufacturers very serious trouble.

A. Langer[2]) reports upon the action of phenolphthalein on American wormseed oil. Langer heats, in a fractionating flask fitted with a descending cooler, a mixture of the oil, phenolphthalein and some toluene up to 175°. The flame is then taken away; the reaction proceeds spontaneously under rise of temperature. After driving off the rests of toluene and terpene by a current of steam, there remains a solid, reddish-yellow cake which is soluble in hot toluene and can thus be separated from the excess of phenolphthalein. The body has the character of a dye-stuff and is said to give a sulphonic acid when digested with sulphuric acid. With 10 g. of oil, 6.5 g. of ascaridole and 4 g. of phenolphthalein enter into reaction. Since several other essential oils and adulterated chenopodium oils do not give this reaction with phenolphthalein, the author suggests that the method might be useful for the recognition of oil-blending. Langer believes, in view of the quantitative proportions he used, that 3 molecules of ascaridole react with one molecule phenolphthalein.

We must question this statement and remark that we regard a molecule of such a constitution as improbable, considering the chemical nature and behaviour of ascaridole. Ascaridole[3]) is known to be a peroxide which undergoes a far-reaching decomposition, or a violent molecular transformation, already when heated to 150°. In order to recognise the presence of ascaridole in wormseed oil it is not necessary to test its behaviour with respect to phenolphthalein. Simple heating is sufficient. If the Langer preparation really represents the reaction product of ascaridole and phenolphthalein, it will have to be considered as a reaction product of the decomposed ascaridole after undergoing molecular rearrangement. For these reasons we doubt that the body can therapeutically have the same action as ascaridole itself.

The 15 acres of Government Cinchona plantation in Bengal of *Chenopodium ambrosioides* gave a yield of $2^1/_2$ maunds per acre (1 maund = 37.324 kg.); the yield of oil was very small. The cultivation experiments made with the same plant in the Government Cinchona plantations of the Nilgiris also had, in spite of all care bestowed upon them, so unsatisfactory a result that commercial advantages cannot be looked forward to[4]).

We take the following notes from an article by P. van der Wielen[5]) "On the culture of *Chenopodium ambrosioides anthelminticum*". The seeds of *Chenopodium ambrosioides anthelminticum* have for a long time already been used in Brazil as vermifuges. In 1895 a German pharmaceutical chemist living in Brazil prepared the essential oil from the seeds of this plant. The oil had been mentioned in the American pharmacopœia, but

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[1]) *Report* October 1915, 41. — [2]) *Pharm. Ztg.* 66 (1920), 191. — [3]) *Report* April 1908, 115; October 1912, 115. — [4]) *Perfum. Record* 12 (1921), 8. — [5]) *Chemist and Druggist* 93 (1920), 1334.

before 1912 nobody would have enumerated it among the indispensable medicines[1]. Only after two Dutch medical men, Schüffner and Vervoort, had ascertained in Deli (Sumatra) that chenopodium oil was a very effective remedy again the hookworm disease[2], the oil became, according to Van der Wielen, the important vermifuge of the present days. At the present time *Chenopodium ambrosioides* is being cultivated in Deli and also in other places of the Dutch East Indies. The plants obtained from Deli seeds have also been cultivated with success in the botanical gardens at the University of Amsterdam.

From the seeds of *Chenopodium ambrosioides,* L., erroneously known also as *American Semen Contra*[3], which come from the Dutch East Indies, Roure-Bertrand Fils[4] obtained by direct steam distillation, 0.7 per cent. of a pale-yellow oil of the following constants:—d_{15° 0.9763; $\alpha_D \pm 0^\circ$; acid v. 0.93; ester v. 6.54; sap. v. 7.47; soluble in two or more volumes of 70 per cent. alcohol. By extracting the distillate with petrolether a further 0.35 per cent. of an oil, more of amber colour and less soluble in alcohol of 70 per cent., was obtained; this oil had the constants:—d_{15° 0.9843; $\alpha_D \pm 0^\circ$; acid v. 0.93; ester v. 13.05; sap. v. 13.98; the solution in 70 per cent. alcohol was turbid.

In distinction from the American wormseed oil which is lævorotatory, this Indian chenopodium oil is inactive. According to Tijssen two Indian oils were even found to be dextrorotary ($\alpha + 0.48^\circ$ and $+ 0.50^\circ$). Nevertheless these oils are reputed good vermifuges and have, according to Schüffner and Tijssen[5] been applied with success against the hookworm disease.

The trade with American wormseed oil still leaves a great deal to be desired. Although the genuine oil is no longer an article as difficult to procure as it was in the past years, the samples which we analysed in our laboratories were still predominantly artificial products, though partly superior to the former articles in sofar as they had been "perfumed" with some genuine oil. We hope to be able to give a more favourable report next year.

There is no objection to the preparation of substitution-products of oils which are manufactured for perfumery, since they meet a demand which has become urgent and since they partly replace the natural oils very well. The case of oils which, like the American wormseed oils, are exclusively for medicinal use is entirely different. As long as we are not able to prepare, by chemical or other means, the ascaridole, the essential or effective constituent—and there is so far no chance of that—talk of the preparation of an artificial wormseed oil is simply a nonsense. For in this case we do not wish to have a product, which more or less resembles the article by odour or taste, but we must have a product which is *equivalent therapeutically.* This, however, could only be the case if the artificial oil contained ascaridole as chief constituents, which appears excluded for the present. It is all the more regrettable when a Hamburg firm, not an important one, it is true, advertises artificial *Ol. chenopodii*; some *bona fide* buyers, believing in the medicinal efficacy of the oil, will be caught by this offer. We presume that the respective firm was not acquainted with the actual conditions and had no idea of the uselessness of such an artificial product. We make these statements merely for the purpose of warning against this artificial oil.

The following communication from E. Merck[6] will show that we are not alone in our bad experience with American wormseed oil. According to this communication an oil advertised by a Hamburg firm as *Oleum Chenopodii artificiale* had the following

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[1] The article does not mention that H. Brüning had recommended American wormseed oil in Germany already in 1906 as a vermifuge, and that we had thoroughly tested it in 1908. — [2] Cf. also *Report* Oct. **1913,** 108; *Report* **1919,** 61. — [3] *Semen contra* = *Semen Cinæ.* — [4] *Bull. Roure-Bertrand Fils,* October **1920,** No. 2, 29. — [5] See also *Report* **1919,** 113. — [6] *Pharm. Ztg.* **66** (1921), 214.

constants: — d_{15° 0.9945; $\alpha_D + 1.3^\circ$; soluble with turbidity in 10 vol. 70 per cent. alcohol. The odour of this oil reminded of anethole and eucalyptole; the comparison with the genuine American wormseed oil which has quite different constants left no doubt that this artificial product has nothing whatever to do with the natural oils, and that it did not contain the active constituent of the genuine oil, ascaridole.

D. A. Roth1) applied the American wormseed oil in more than 100 cases of uncinariasis and observed in 30 per cent. of the cases concomitant effects, such as giddiness, sick feeling, vomiting, headache, deafness and general depression. In more than 20 per cent. of these cases the deafness2) was more or less severe, and in the case of four patients it persisted after two years. The application of thymol did not cause similar phenomena. The author, therefore, warns against applying wormseed oil to highly-anaemic persons. The medication should not be repeated before the expiration of ten days. A blood test and a determination of the contents of hæmoglobin would further be advisable.

A serious case of ascaridiasis with ileus, which was not to be cured by santonin, was effectively treated by Steber3) by applying three times a day eight drops of American wormseed oil and subsequently castor oil.

We have repeatedly discussed cases of poisoning by American wormseed oil4). An extensive memoir on this subject has recently been published by A. Preuschoff5). The numerous experiments with this oil made on animals had already proved that this remedy is not free of danger and may prove fatal, if applied in too large quantities. Within the years 1851 to 1919 24 cases of poisoning had been observed in 9 adults and in 15 children; of these five grown-up people and nine children died. In many cases the accidents were to be traced to the fact that the usual doses for worms had much been exceeded. Frequently, moreover, the improper way of applying the worm cure was responsible for the injury; sometimes the patients had already been weakened by other illnesses, or the wormseed oil had been applied mixed with other essential oils (oil of turpentine), or it had been applied without the addition of aperients. Idiosyncrasy must by considered a third cause for poisoning by wormseed oil.

The adulteration of the oil with other oils, about which nothing is known in the cases just mentioned, may have serious consequences. Experiments made on animals have proved that already small doses of anise, rosemary and lavender oils may prove fatal.

In the opinion of the author the American wormseed oil need not be eliminated from our lists of remedies. Cases of poisoning would, it may safely be stated, be impossible if the oil were applied strictly according to the injunctions of Brüning6).

Wormwood Oil.—As regards Spanish wormwood oil see page 82 of this *Report*.

Ylang-Ylang Oil.—As regards Ylang-Ylang oil from the Philippines, see page 84 of this *Report*.

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1) *Southern Medical Journal*, November 1918; *Journal of Tropical Medicine and Hygiene* No. 1 (1918), 16. From E. Merck's *Jahresbericht* 31 to 32 (1917/18), 364. — 2) Cf. *Report* 1919, 62. — 3) *Deutsche med. Wochenschr.* No. 33 (1917), 1040. From E. Merck's *Jahresbericht* 31 to 32 (1917/18), 364. — 4) Cf. *Report* October 1915, 43; 1919, 62. — 5) *Zeitschr. f. exp. Pathologie u. Therapie* 21 (1920), No. 3, p. 1. Reprint was kindly sent to us. The oil is not obtained, as the author writes, only from the fruit of *Chenopodium ambrosioides* L. var. *anthelminticum* Gray, but from the whole plant. — 6) Cf. *Report* 1920, 61.

Chemical Preparations and Drugs.

Benzyl Alcohol. — According to D. I. Macht1), benzyl alcohol, already recommended as a local anæsthetic2), is also a good remedy against toothache. The alcohol is said to remove the pain at once, when dropped on cotton wool and placed in the hollow tooth, alone or mixed with chloroform. The remedy is considered less poisonous than other anæsthetics and therefore valuable.

Benzyl benzoate has for some time been applied in cases of spasms of the plain muscular fibre3). Macht and Litzenburg4), as well as Cheinisse5), recommend it in cases of peristaltic inflammation of the intestines, in dysentery and other enteritis, in post-operative spasms of the intestines, in spasmic obstipation, in colic of the gall and kidneys and spasms of the bladder.

Treatment with benzyl benzoate was successful with dysmenorrhoea in 81 per cent. of the cases, with bronchial asthma and also with croup in most instances.

In general five to forty drops of 20 per cent. alcoholic solution are applied in water perorally. In addition of 1 to 5 per cent. of benzaldehyde is said to increase the effect in cases of croup.

T. E. McMurray6) also obtained good and rapid success with benzyl benzoate without observing any deleterious consequences. D. I. Macht7) cured obstinate cases of hiccough with the ester, when other external and internal remedies had failed. He believes that benzyl benzoate is valuable also for the diagnosis, because it admits of drawing a distinction between hiccough of purely-central and hiccough of more peripheric origin. Since this remedy acts in the main peripherally upon the plain muscles, it should be especially effective in dealing with cases of hiccough of peripheral origin. Twenty to forty drops of an alcoholic solution should be given to the patient in water or in milk. The use of benzyl benzoate-capsules is not advisable. Macht reports further that the remedy also expands the blood vessels and does not attack the heart; angina pectoris was treated with success.

According to experiments which E. A. Heller and E. Steinfield8) had been making with rabbits, benzyl benzoate has, by contrast to benzene, no toxic effect on leucocytes.

Benzaldehyde. — The method for the determination of the chlorine contents in benzaldehydes, which we mentioned in last year's *Report*9), has meanwhile been perfected, and the research has been brought to a certain conclusion.

We conducted the combustion originally in a large glass flask which was being fed with oxygen. Having in further experiments succeded in constructing a lamp in

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1) *Americ. Journ. Pharm.* **93** (1921), 52. — 2) Cf. *Report* **1919**, 66. — 3) *Therap. Halbmonatsh.* **34** (1920), 651. — 4) *Journ. Americ. Med. Assoc.* **73** (1919). — 5) *Presse médicale* **1920**, 717. — 6) *New York Med. Journ.*, 24. VIII. **1920**, p. 122. From *Americ. Journ. Pharm.* **92** (1920), 926. — 7) *Med. Record*, 24. VII. **1920**, p. 146. From *Merck's Report* **30** (1920), 7. — 8) *New York med. Journ.*, 31. VII. **1920**, p. 160; from *Americ. Journ. Pharm.* **92** (1920), 916. — 9) *Report* **1920**, 64.

which it is possible to burn the benzaldehyde with a non-sooting flame by supplying air, we have replaced the flask by a vertical glass cylinder through which we draw a current of air which is free from hydrochloric acid.

We have found a suitable medium for the absorption of the hydrochloric acid, resulting from the combustion of the chlorine compounds, in a very diluted potash lye, of which a sufficient quantity is placed into the first absorption vessel, of the apparatus, a U-tube charged with glass beads. The second absorption vessel which contains the same amount of caustic lye, but is charged with glass beads only in the one limb, enables us to control whether the total amount of hydrochloric acid has been retained in the first absorption vessel. There is further a test tube, partly filled with water and provided with a suction nozzle, for the purpose of making a qualitative test of the abscence of hydrochloric acid in the drawn-off gases of combustion.

The annexed diagram will explain the construction of the apparatus¹). We should state that only the U-tubes E and F are clamped, both to the same stand, by the two limbs which are next to one another, whilst the combustion cylinder D and the sphere G find sufficient support by their stoppers.

The most important part of the apparatus is the lamp A, in which the material is burnt and which is mounted on a flask of a capacity of about 20 cc. The neck of the flask is provided with two ground-glass joints, the one on the outside for the cap B which is put on when a weighing is to be made, and the other on the inside. There a glass tube, slightly thicker at its lower end, is ground into the neck. Into this tube fits a small tube of porcelain which is likewise thickened just below its upper end. This porcelain tube which has an internal diameter of 2 mm. carries the asbestos thread A which serves as a wick. On the upper portion of the glass tube fits a short sleeve of metal threaded on the outside; the sleeve is pushed over the thickened portion of the glass on which it sits firmly. The three-arm spider for the semispherical globe which is fitted with an aperture of 6 mm. turns easily on the threaded sleeve.

Before we proceed to a quantitative determination the respective benzaldehyde is first tested qualitatively for its chlorine contents²) in order to obtain some indication of the quantity of material to be burnt in the test. The apparatus is then fixed up for the quantitative estimation in the following way:—

The two limbs of the tube E are charged with glass beads to about three quarters of their length, and 25 cc. of N/50 caustic potash are introduced through the upper opening, into which the cylinder D is afterwards fixed, so that the beads of the limb are wetted with the potash. The one limb of the U-tube F is then similarly charged with glass beads and with the same amount of caustic potash. Both the U-tubes are now clamped in their upper portions and are closed by their rubber stoppers. The test tube H is charged with about 10 cc. of water and joined to the sphere G which is fixed in position on the top of the tube F; H is then connected with the water jet pump. Finally the combustion cylinder D is joined to the U-tube E, and the lamp holder is preliminarily fixed by means of its holder C and the stopper pushed over C. As the air of the laboratory might contain some vapours of hydrochloric acid, the holder C is connected with a washbottle containing diluted silver nitrate; the water jet pump is started at a rate that about 1 litre of air is drawn through the apparatus a minute.

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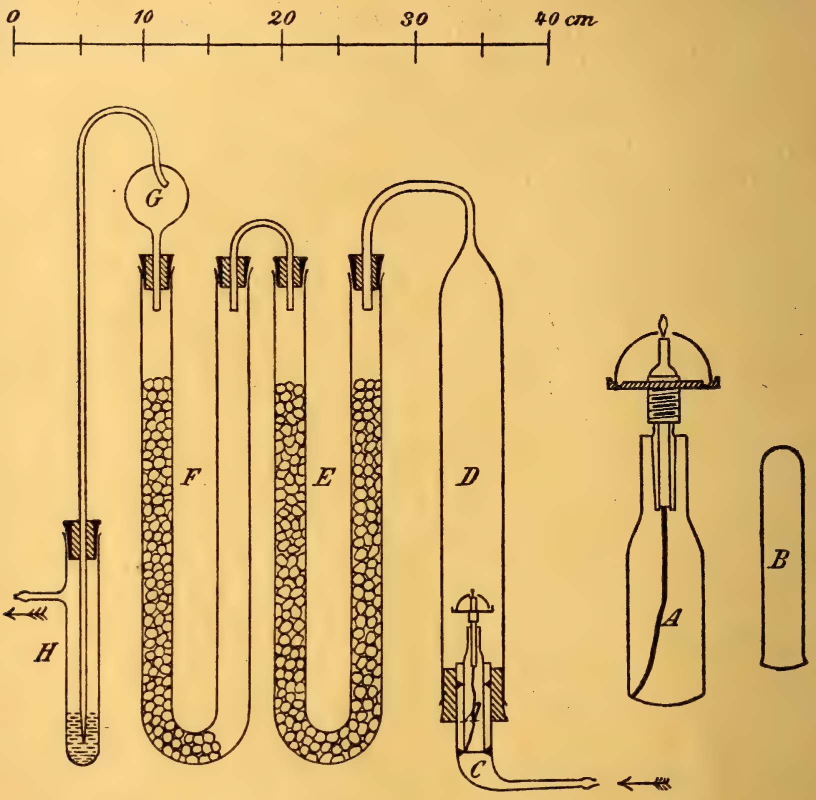
¹) The apparatus can be obtained from F. Hugershoff in Leipzig. — ²) Gildemeister and Hoffmann, *The Volatile Oils*, vol. I, p. 609, and *Report* October 1904, 8.

We now fill the lamp with the benzaldehyde to be tested, close it by the burner from which the asbestos wick will project by about 2 mm., put on the cap *B* and weigh. Having taken the cap off again the threaded sleeve and globe-spider are pushed over the glass tube, the globe is put on and its height is so adjusted by turning the spider, that the opening of the globe extends only a little higher than the end of the asbestos wick. The lamp is now mounted in its holder, in which it will rest on the three lower large inward projections, whilst the three upper and smaller projections keep an even annular distance between the lamp and the wall. The benzaldehyde is lighted, and the vessel and lamp are at once brought under the cylinder *D*. The height of the flame is adjusted to 6 or 7 mm., if necessary by turning the globe spider, and attention is paid to the non-appearance of any soot. With this size of flame about 1 g. of benzaldehyde will be consumed per hour. The stopper *C* is then tightly pushed into the cylinder *D*, and the connection with the wash bottle is re-established for maintaining the circulation of the air, if this connection should have been interrupted. By means of a screw pinch cock pushed over the rubber tube the air supply is regulated; it has been proved to be advantageous to let the water-jet pump draw briskly, lest the flame be extinguished with insufficient draught. The air feed will be sufficient when no water is deposited on the wall of the combustion cylinder. Should the absorbing liquids begin to foam strongly, a few drops of petroleum are put in to the U-tube.



If, with prolonged combustion, the flame size should diminish owing to charring of the tip of the wick, the vessel *C* and the lamp are taken out, after partly screwing down the suction pump, lest the opening of the apparatus should drive the absorption liquids back into the apparatus. The lamp is weighed as before; the asbestos wick is pulled out by means of pincers, 2 or 3 mm., and the charred tip is cut off with the scissors. A second weighing will show the loss of weight thus produced; the apparatus is re-erected and the combustion continued.

When a sufficient quantity of benzaldehyde has been burnt, the lamp is taken out, and the weight of the consumed benzaldehyde is ascertained. After passing an air current at moderate rate for some time through the apparatus, the joint is loosened below the sphere *G*, and the water-jet pump is stopped.

In order to remove any petroleum added and any soot that should have formed, the absorption liquids are filtered through glass wool. For this purpose two glass funnels, about 12 cm. diameter, are partly charged with glass wool after fitting a short piece of rubber tubing provided with a pinch cock over the funnel tube. The funnels are attached to the stand, and two Erlenmeyer flasks of about 500 and 350 cc. capacity are placed under the funnels. The cylinder *D* is taken off, the short connections between the two tubes are removed, and the content of each U-tube is emptied into one of the funnels after opening the pinch cocks, the U-tube *E* being discharged into the larger Erlenmeyer. When the liquid has completely drained off, the pinch cocks are closed, and each U-tube is rinsed with 15 cc. of water three times and the cylinder *D* twice, this water being added to the funnel contents (the cylinder wash water into *E*). If the beads on the funnels should not quite be covered with water, a suitable amount of water is added; the pinch cocks are opened a few minutes afterwards. This washing of the glass beads is repeated 3 times so that the liquid will amount to about 300 or 200 cc. We now add 50 cc. of N/50 sulphuric acid to each of the two Erlenmeyer flasks and also a few marbles, to ensure quiet boiling; the flasks into which small funnels are fitted are then heated on asbestos wire netting until the liquid has been concentrated down to 25 cc. After cooling we titrate, after additionof a little phenolphthalein as indicator, with N/50 caustic potash until the colour remains red; the amount of potash is noted. We then destroy the red colour again by means of one or two drops of N/50 sulphuric acid. Now follows, after addition of 5 drops of 10 per cent. potassium dichromate solution, titration with N/50 silver nitrate, first of the liquid from the U-tube *F* which served for control, until a faint chromate colouring becomes visible, and then of the contents of the second Erlenmeyer.

In control tests, conducted in the same way for ascertaining the chlorine contents of the water and of the standard solutions, we used the same amount of caustic potash and of silver nitrate as the contents of the U tube *F* had required (0.4 cc.). It was thus proved that the whole of the hydrochloric acid is really absorbed in the U tube *E*, and that we need, in our calculations, only consider the silver nitrate that was wanted for the contents of U tube after deducting the control amount. Since now 1 cc. of N/50 silver nitrate corresponds to 0.00071 g. of chlorine, the chlorine contents of the respective benzaldehyde would be:—per cent. chlorine $= \alpha \cdot 0.071/s$, where α denotes the number of cc. of N/50 silver nitrate used and s the weight of benzaldehyde burnt, in g.

In order to check the reliability of the method we conducted experiments with natural bitter almond oil, containing prussic acid and free of prussic acid, with artificial benzaldehyde and with benzaldehyde of known chlorine percentage.

We tabulate the results of these experiments.

material	weight burnt g.	chlorine per cent.
bitter almond oil (own distillate), prussic acid, faint	9.94	none (0.000)
" " " " " " " strong	7.99	none (found 0.004)
" " " " " " " none (natural benzaldehyde)	7.24	none (found 0.001)
benzaldehyde, artificial	5.77	0.01
" "	7.01	0.009
" "	11.8	0.007
the same benzaldehyde + 1 per cent. chlorine (as monochloro benzene)	1.05	1.02
" " " + 1 " " "	1.72	1.03
" " " + 1 " " "	1.98	1.02
" " " + 0.5 per cent. chlorine	2.16	0.52
" " " + 0.5 " " "	2.68	0.51
" " " + 0.1 per cent. chlorine	2.615	0.105
" " " + 0.1 " " "	4.15	0.108
" " " + 0.033 per cent. chlorine	9.95	0.039
benzylacetate	8.02	0.005
" with a little chlorine	3.31	0.029

Whilst the combustion of the materials of these experiments gave no trouble, we had to make an addition of some 95 per cent. of spirit (alcohol) in the case of an anise aldehyde which had been mixed with 1 per cent. of chlorine. In this case the same quantity (by weight) was used of anise aldehyde and of spirit, and the combustion of 0.87 g. of this mixture yielded 0.54 per cent. of chlorine, corresponding to 1.08 per cent. of anise aldehyde free of alcohol. The consumption of normal potash solution may, like the consumption of the silver nitrate solution, be utilised for the estimation of the chlorine contents, since in the experiments made the two values accorded with one another, except in the case of the bitter almond oils containing prussic acid, in which case the consumption of lye was considerably greater than the consumption of the silver nitrate, a difference which is obviously to be traced back to the prussic acid[1]).

In the course of the last six months we have had repeated opportunities to test benzaldehydes of guaranteed chlorine contents, as well as bitter almond oils, "genuine" and free of chlorine, by the method just described, and we might state, on the strength of the values found, that scarcely a single one of the samples investigated accorded with the statements of the respective suppliers. In some cases the discrepancies were very considerable, and we can only explain them by assuming that only the chlorine of the side chain was taken into consideration in the tests, but not the chlorine of the nucleus.

material	quantity used g.	chlorine per cent.
benzaldehyde, free of chlorine	7.75	0.025
" not more than 0.002 per cent. chlorine	4.20	0.015
" nearly free of chlorine	3.34	0.036
" technical	4.425	0.122
" not over 0.002 per cent. chlorine	2.44	0.20
" less than 0.02 " " "	2.16	0.40
" " " 0.02 " " "	1.56	1.04
bitter almond oil, genuine, free of prussic acid	6.2	0.035
" " " " " " " "	7.6	0.054
" " " " " " " "	2.94	0.18

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[1]) We revert to this point further on.

The just-described method will, we think, remove a difficulty which has meanwhile made itself very much felt. The uncertainty of obtaining a benzaldehyde really free of chlorine in a commercial way had become intolerable since preparations had been put on the market labelled "technically free of chlorine". The qualitative test was sufficient to show that these materials still contained very considerable amounts of chlorine (compare table above); yet these materials found buyers when the sellers had sufficient audacity to assert that their product did not contain more than 0.02 per cent. of chlorine, which was accepted as the maximum permissible contents of an aldehyde "technically free of chlorine". Up to the present they might risk such bold assertions in the knowledge that most analytical chemists were not in a position to establish the chlorine contents beyond doubt. As a striking proof for the correctness of this assumption we give the following summary of data placed at our disposal; they concern the amounts of chlorine found in 4 different commercial laboratories in four different samples of benzaldehyde. Our retesting by the method described gave in all the four samples chlorine percentages which exceeded the double values found by other methods.

	Laboratory				Schimmel & Co.	
	I per cent.	II per cent.	III per cent.	IV per cent.	material burnt g.	chlorine per cent.
Benzaldehyde I	—	0.01	0.19	0.18	3.26	0.44
„ II	—			0.08	3.06	0.13
„ III	—	0.02	0.11	0.12	3.46	0.33
„ IV	0.06				4.05	0.26

Since we can burn any desirable quantities of benzaldehyde in the manner described, even low chlorine contents may accurately be determined, and it is now really possible to identify a benzaldehyde free of chlorine as such. Our experiments demonstrate that the limit of sensitivity is about 0.005 per cent. of chlorine. When the values go below that, the consumption of silver nitrate, amounting only to a few drops, will be too small to give reliable results, all the more so, because bitter almond oils of our own manufacture (see page 56), both containing prussic acid and free of prussic acid, the absolute freedom from chlorine of which we were able to guarantee, consumed a few drops of silver nitrate, a quantity which may hence be neglected. *Painfully-careful testing* presumed, we may therefore designate a benzaldehyde as free from chlorine with all certainty, when the method mentioned yields, in the combustion of about 8 or 10 g. of benzaldehyde, values which are below 0.005 per cent.

In the same way as for the purpose outlined, the method may be found to be quite generally suitable technically for the quantitative estimation of the halogen contents of organic halogen compounds. That would be an advantage over the method of Carius since our determination is more convenient and takes less time. With easily-combustible materials there will be no trouble in the combustion. Solid bodies and substances which are not easily combustible would have to be mixed with alcohol or some similar material. We intend to pursue these experiments.

Borneol.—According to an English journal[1]) ordinary camphor may be replaced by Ngai camphor with advantage, especially for industrial purposes. So far the expensive Ngai camphor, which comes from a weed growing abundantly in Assam and Burma and which consists almost entirely of pure *l*-borneol, had only been used in China for the manufacture of scented Chinese inks[2]). The high price, which had to be paid

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[1]) *Chemist and Druggist* **92** (1920), 910. — [2]) Cf. *Report* **1920**, 67.

for this product[1]), altogether used to exclude its application as a substitute for camphor. Since, however, the ordinary camphor has risen to more than ten times its price, the industry of Ngai camphor may have a future.

Bromostyrene.—A bromostyrene, submitted to us for our examination, proves once more how careful one should be with so-called "priceworthy" products. We tabulate its properties found and those of a technically-pure bromostyrene:—

	Sample	Pure bromostyrene
d_{15°	1.5015	1.41 to 1.43
Solubility in 90 per cent. alcohol	5 vol. and more	4 to 5 vol.
Solidification point	did not solidify even at −20°	±0° to −2.5° (cooled down to −7°).

It will at once be seen that the preparation was altogether of inferior quality. The specific gravity is far too high, and the characteristic property of bromostyrene, to freeze at 0° or a little below, is missing.

The examination did not reveal any indication of an aulteration. The product seemed merely to be highly impure, which is just as unpleasant, of course, for the consumer. It need hardly be said that the inferior quality was likewise obvious in the odour.

Camphor.—The Japanese export figures for the year 1920 being now available we give a comparative table of the weights and values of the last three years:—

	1918 kin	1919 kin	1920 kin
British India	361179	67521	395728
Great Britain	383911	175317	133859
France	90904	146222	28583
United States	595622	1569506	294007
Australia	94946	2026	28322
Other countries	238155	70688	153063
kin	1764217	2031280	1033567
value in yen	3686375	7883875	4965350

An article by E. Witte[2]) discusses the patent literature on the synthesis of camphor. The author briefly reviews the processes by means of which pinene has been converted into camphor *via* pinene hydrochloride, camphene, *iso*bornylester, and *iso*borneol, and he gives at the same time a detailed table, classified in groups, of all the patents concerning the synthesis of camphor.

In experiments made on rabbits H. E. Sigerist[3]) came to the conclusion that the chronic application of camphor did not do any harm to the heart of the normal animal. The muscles of the left and right ventricle seemed even to be able to adapt themselves to increased efforts. This result of Sigerist has been confirmed by Th. Zangger[4]) in the treatment of chronic myocarditis. Within the last ten years he has treated some hundred patients with spirits of camphor applied internally, two or three times daily, in doses of ten to fifteen drops.

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[1]) According to M. Rondot *"Etude Pratique du Commerce d'Exportation de la Chine"*, Paris **1848**, the pikul (133⅓ lbs.) of Formosan camphor was, in 1848, valued at 25 \$, of Japanese camphor at 30 \$, of Ngai camphor at 250 \$ and of Borneo camphor at 1000 \$. — [2]) *Chem. Ztg.* **45** (1921), 118. — [3]) *Korrespondenzblatt f. Schweizer Ärzte* **47** (1917), 1748. — [4]) *Ibidem* **47** (1917), 1752.

Astonishing success has been obtained by F. M. Groedel[1] with camphor in various pure and combined nervous disturbances of the circulation. He found it advantageous to inject subcutaneouly at first 0.5 to 2, even up to 4 cc. of a 20 per cent. solution daily, and later on to apply 0.1 to 0.2 g. taken internally. Very large doses of camphor might cause convulsions, but they would be harmless in the opinion of the author.

In the place of the 20 per cent. oil of camphor Leo[2] recommends the 0.142 per cent. solution of camphor free of alcohol in Ringer's solution. This camphor water was intravenously injected in order to stimulate breathing and the action of the heart.

In grave cases of bleeding from the lungs E. Boit[3] injected up to 10 cc. of a 10 per cent. oil of camphor subcutaneously; he found that single maximum doses of 2 g. of camphor and maximum daily doses of 4 g. could be borne without detriment.

Feer[4] has likewise applied large doses of camphor in cases of influenza-pneumonia.

In cases of infections broncho-pneumonia of horses N. Hillerbrand[5] injected two or three times daily 200 cc. of camphor-water intravenously. The fever disappeared then, and the disease proved curable.

By comparative experiments with *d*-, *l*-, and *i*-camphor Joachimoglu[6] came to the conclusion that the three kinds of camphor are pharmacologically equivalent.

In cases of heart weakness, up to ten grains (about 0.6 g.) of camphor may according to an English report be injected at the time, dissolved in oil. Such doses are painful but very effective[7].

By experimenting with isolated, surviving hearts of rats A. Fröhlich and L. Pollak[8] studied the action, so far not fully explained, which camphor has on the hearts of warm-blooded animals. According to these researches camphor favourably influences the action of hearts weakened by the lowering of temperature, by electric shock, poisoning with phosphorus, and with preparations of digitalis, yohimbin or chloroform. In these cases the peripheral vagus stimulations were absent; they observed, moreover, an increasing frequency and sometimes also a regularisation. When, however, the coronary circulation was impaired, the favourable influence of camphor upon the action of the heart frequently failed likewise. When the circulation with a liquid containing camphor was replaced by one without camphor, the pathological action of the heart again made its appearance. The clinical observations corresponded to the pharmacological results.

When camphor was combined with remedies expanding the vessels like coffeine and papaverine the favourable action upon the heart was intensified. These experiments thus demonstrate that the combination of the coffeine and camphor-therapy, which is frequently applied in practice, is quite justified.

Cinnamein.—A so-called artificial cinnamein had been submitted to us for detailed examination because it did not admit of preparing a concentrated solution of artificial musk, such as the natural product will yield. The analyses made in our laboratory

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[1] *Therapie der Gegenwart* No. 4 (1917), 120. — [2] *Deutsche med. Wochenschr.* No. 11 (1918), 285. — [3] *Beiträge zur Klinik der Tuberkulose* 37 (1917), No. 1 to 2. — [4] *Korrespondenzblatt f. Schweizer Ärzte* No. 48 (1918). — [5] *Münchener tierärztl. Wochenschr.* No. 35 (1917). — [6] *Arch. f. exp. Pharm. u. Path.* 80 (1917), 259; 282. All these references (2 to 9) are abstracted from E. Merck's *Jahresbericht* 31 to 32 (1917 to 1918), 214 to 217. — [7] *Brit. Medical Journ.* 1920, 828. From *Chem. Zentralbl.* 1920, III. 393. — [8] *Arch. f. exp. Pharm. u. Path.* 86 (1920), 104. From *Chem. Zentralbl.* 1920, III. 260.

at once accounted for the different behaviour. It was established that the artificial product consisted to about 70 per cent. of glycerin acetate, and that it seemed to contain in the rest esters of the cinnamic acid, since the acid separated from this fraction was identical as to melting point (133°) with cinnamic acid. To judge by the sweetish taste methyl or ethyl esters of cinnamic acid had found application.

A product of this constitution can naturally not be a suitable substitute for cinnamein, and we must not be surprised when it proved unsuitable for the intended preparation. People must not take matters too easily in the preparation of artificial products. It is by no means sufficient to pour some things together, without any actual knowledge of the conditions, and then to give the creation some name. Particularly reprehensible are these products however, when a good substitute for the respective oil is at disposal, such as benzyl benzoate, which is the main constituent of the natural cinnamein and which might, therefore, rightly be called artificial cinnamein.

Cinnamic Aldehyde.—Referring to a book of A. Landerer *"Die Behandlung der Tuberkulose mit Zimtsäure"* (The Treatment of Tuberculosis by means of Cinnamic Acid) (1898) A. Phillipson[1]) publishes the experiences which he made in treating lupus and scrofulous glands with cinnamic aldehyde. Landerer had found that Peru balsam, which had been applied with success in surgical tuberculosis, owed its efficiency to the cinnamic acid. The simple preparation (cinnamic acid) acted with intravenous introduction quite as favourably upon tuberculous growth as the complex preparation (Peru balsam). On external application, however, the cinnamic acid proved little efficient in surgical tuberculosis. For this reason Landerer applied in such cases only Peru balsam or cinnamyl*meta*cresol. Phillipson could confirm that Peru balsam was much more efficient with external tuberculosis than cinnamic acid and its derivatives. He found, however, a good substitute for the balsam in cinnamic aldehyde which has recently also been much applied against scabies[2]). For local treatment of external tuberculosis a cotton wool pad, moistened with 1 per cent. aldehyde water, was twice daily placed for one hour upon the affected spot. The cinnamic aldehyde always called forth strong hyperæmia, leucocytose and exudation and initiated the restoration of the tissues without any loss. The author describes fully several cases in which he was able to cure serious lupus in this way without any surgical help.

Civet.—The news about the civet trade is not pleasing. It looks almost as if unadulterated civet were no longer procurable. We had at any rate great difficulty in obtaining any pure material. The samples which we collected for this purpose from otherwise reputed firms of England, France and Germany were almost throughout falsified, and in most instances, as the subjoined table will show, to a very considerable extent. The examination was mostly effected by the method which we described on page 69 of our last *Report* and may here briefly be summarised again. 5 g. of civet are fused in an acetylation flask on a water bath and extracted successively with 90 per cent. alcohol, ether and chloroform. The extracts are collected in separate saponification flasks, the solvents are distilled off, the residue is for some time placed in a vacuum desiccator, and the weight and the acid value and ester value are then determined. The weight of the portion of the civet which has not been dissolved is likewise determined. The water percentage is deduced from the difference between the applied quantity of civet and the extracts plus the insoluble residue. An incineration

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[1]) *Therap. Halbmonatshefte* **34** (1920), 356. — [2]) Cf. *Report* **1917**, 90.

of the insoluble residue further gives information concerning the proportion of inorganic constituents in the civet. We have so far observed the following figures in good commercial articles.

	Per cent.	Acid value	Ester value	Sap. value
Alcohol extract . .	45.8 to 58	118.2 to 147.3	29.0 to 53.0	155.4 to 182.8
Ether extract . . .	12.6 „ 19.9	7.9 „ 18.0	64.9 „ 89.7	75.9 „ 96.9
Chloroform extract .	0.3 „ 6.4	5.9 „ 20.0	78.0 „ 155.0	98.0 „ 160.9
Residue	5.4 „ 9.5	—	—	—
Water	13.5 „ 21	—	—	—
Ashes	1.09 „ 2.15	—	—	—

The analytical results of the above-mentioned samples which we subjoin were very different from the figures given. The discordant values have been distinguished by bold type to make them more conspicuous; no notice has, however, been taken of minor discrepancies which might bee due to defects of the methods applied.

Civet, adulterated.

No.	Extract: Alcohol				Ether				Chloroform				Residue	Water	Ashes	Mode of adulteration
	p. c.	A. V.	E. V.	S. V.	p. c.	A. V.	E. V.	S. V.	p. c.	A. V.	E. V.	S. V.	p. c.	p. c.	p. c.	
1.	**28.4**	122.3	38.7	161.0	**25.2**	6.7	**28.0**	**34.7**	0.2	—	—	—	**16.9**	**29.3**	1.2	Vaseline, organic substance, water
2.	**30.6**	119.3	31.2	150.5	**29.2**	10.5	**38.9**	**49.4**	2.0	8.4	111.9	120.3	**15.4**	**22.8**	1.0	vaseline, organic substance, water
3.	**34.6**	127.8	33.2	161.0	**9.3**	21.1	66.2	87.5	0.1	—	—	—	**49.3**	**6.7**	**43.0**	talcum
4.	**43.8**	120.9	**17.9**	**138.8**	**38.2**	13.2	**34.4**	**47.6**	4 3	6.5	97.7	104.2	6.6	**7.1**	—	vaseline
5.	**29.8**	**101.0**	**16.8**	**117.8**	**53.9**	8.4	**30.5**	**38.9**	7.2	—	—	—	6.8	**2.3**	—	vaseline
6.	**26.9**	120.8	50.0	170.2	**27.6**	6.1	**26.4**	**32.5**	0.3	—	—	—	**16.8**	**28.4**	1.04	vaseline, organic substance, water
7.	**28.3**	130.6	39.6	170.8	**23.2**	18.2	**40.6**	**58.8**	0.5	—	—	—	**17.6**	**30.4**	—	vaseline, organic substance, water
8.	**29.8**	122.2	32.0	154.2	**25.8**	9.8	**35.8**	**45.6**	2.3	12.2	97.4	109.6	**16.0**	**26.1**	1.2	vaseline, organic substance, water
9.	**41.4**	—	—	—	**41.6**	—	—	—	3.4	—	—	—	5.8	**7.8**	—	vaseline
10.	**41.5**	119.1	36.9	156.0	12.5	**28.0**	**56.0**	84.0	0.5	—	—	—	**20.2**	**25.3**	1.5	vaseline, organic substance, water
11.	**35.3**	115.8	38.9	154.7	12.8	**26.2**	65.6	91.8	0.3	—	—	—	**45.0**	**6.6**	**39.0**	talcum
12.	**33.3**	—	—	—	13.4	—	—	—	0.2	—	—	—	**44.9**	**8.2**	—	organ. substance
13.	**34.0**	—	—	—	10.8	—	—	—	0.2	—	—	—	**48.7**	**6.3**	—	organ. substance
14.	**33.5**	128.7	29.2	157.9	11.0	20.4	68.7	89.1	0.5	—	—	—	**48.1**	**6.9**	**42.2**	talcum
15.	**37.6**	119.9	53.6	173.5	19.6	**28.6**	71.4	100.0	0.6	—	—	—	**19.3**	**22.9**	1.7	vaseline, organic substance, water

This table gives a sad picture of the position of the civet trade. Vaseline figures in the first place among the additions. People have not at all been shy in that respect; for vaseline has been added up to nearly 50 per cent. (sample 5). More frequently we meet with organic substances, about the nature of which we can only affirm that they did not consist of starch. The water percentage, very high in some cases, indicated that in several instances water must actually have been added. Talcum has only three times been met with, but then in quantities which could not be called modest, since they approached 40 per cent.

Will a better state of affairs once more be established? We will not give up the hope.

In analysing a so-called pure sample of civet J. Nivière¹) observed the following:— 83.6 per cent. of the substance were soluble in cold benzene, 57.01 per cent. in cold 96 per cent. alcohol. In the portion which was insoluble in alcohol cholesterol was detected by means of the Liebermann reaction. The portion soluble in alcohol had the constants:—acid v. 106.3; ester v. 22.1; sap. v. 128.4; it contained most probably, to judge by the smell, caproic and caprylic acids, a hydroxy-acid (m. p. 70°) of the character of lanopalminic acid, volatile bases smelling of ethylamine and propylamine and scatole. In the portion insoluble in benzene was found a great deal of dextrose. The author supposes that the civet was adulterated with lanoline and sugar syrup. Another sample of civet, analysed by Nivière, contained 18 per cent. of talcum.

Coumarin.—The Tonka beans are an important export article from Trinidad. They are mainly shipped via Port of Spain to the United States, in smaller quantities also to Europe, France and Germany²). In America the beans are chiefly utilised as an addition in the manufacture of tobacco, whilst they find in Europe more application in the perfumery industry. The beans gathered in the forests of the Rio Cauro and Orinoco in Venezuela are shipped to Trinidad, where they are submitted to a special curing process³) before being exported.

In the year 1917, 752601 lbs. of tonka beans of a value of 472055 dollars, in the year 1918 only 19213 lbs. of a value of 11439 dollars, and in the year 1919 171500 lbs. of a value of 167221 dollars were exported to America. A further increase in the exports is expected for 1920.

Em. Bourquelot and H. Hérissey⁴) confirmed by a series of experiments the assumption that coumarin is present in plants like *Melilotus officinalis,* Willd., *Melilotus arvensis,* Wallr., *Melilotus leucantha,* Koch and *Asperdula odorata,* L. in the shape of a glucoside. The plants, killed in hot water or alcohol, did not yield any coumarin, or only traces of it, when distilled. When, however, some acid or some ferment powder, prepared from the fresh plant, or some emulsin had been added in the same experiments before the distillation, considerable quantities of coumarin were found in the distillate. Emulsin caused a change in the sense of the optical rotation in the aqueous extract of the dead plant, as well as an increase in the reducing power. The discrepant results, which the different kinds of plants yielded indicated that the glucosides of the various plants were different or were accompanied by other glucosides likewise hydrolysable by emulsin. The sugar which is liberated at the same time as the coumarin is *d*-glucose (dextrose). It is not certain, however, whether any other bodies are present in addition to these two compounds.

In the leaves of the labiate *Melittis Melissophyllum,* L., which is frequent in the forests of the neighbourhood of Paris, P. Guérin and A. Goris⁵) could establish the presence of coumarin (m. p. 67 to 68°). The characteristic smell of this substance was only noticed after the leaves had been dried or had been exposed to the vapours of chloroform or ether. It may be assumed that the coumarin is present in the plant as a glucoside, and is only liberated by the action of an enzyme likewise found there.

We have years⁶) ago proved the presence of coumarin in the oil of lavender, likewise derived from a labiate.

That coumarin is found in nature mostly in the combined condition had repeatedly been observed already (by Guérin and Goris in *Melittis Melissophyllum,* by Bourquelot

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¹) *Bull. Soc. chim.* IV. 27 (1920), 794. — ²) *Perfum. Record* 11 (1920), 332. — ³) Cf. *Report* 1916, 70. — ⁴) *Compt. rend.* 170 (1920), 1445. — ⁵) *Ibidem* p. 1067. — ⁶) Cf. *Report* October 1900, 41; April 1903, 49.

and Hérissey in *Asperula odorata* and in *Melilotus* species). According to O. von Lippmann[1]) a glucoside containing coumarin occurs also in a variety of *Melilotus arvensis* which grows in Central Germany on railway embankments. The glucoside itself has so far not been isolated, but the coumarin was obtained and characterised after treatment of the expressed juice with emulsin.

As regards the *solubility* of coumarin in water and glycerin, see page 95 of this *Report*.

As regards an *adulteration* of coumarin with magnesium sulphate, cf. p. 76 of this *Report*.

Eucalyptole.—Some years ago J. Belluci and L. Grassi[2]) investigated a number of different compounds which cineole forms particularly with phenol bodies, such as α- and β-naphthol, *o-*, *m-* and *p*-cresol, pyrocatechol, thymol &c. Recently T. Tusting Cocking[3]) has prepared the addition-product of cineole and *o*-cresol again in a pure condition, and has further investigated it. This compound which he calls cresineol is at once deposited in crystals when cineole acid *o*-cresol are mixed in molecular proportions. It has the following properties:—m. p. 55.2°; $d_{60^\circ}^{60^\circ}$ 0.9661; n_{D60° 1.4846; soluble in ether, alcohol and in all organic solvents.

Starting from this investigation the author has worked out the following method for the quantitative estimation of the cineole contents in eucalyptus oil by a cryoscopic test, making use of cresineol:—3 g. of eucalyptus oil are mixed with 2.1 g. of *o*-cresol. From the solidification point of this mixture the required value is deduced by means of a graphic table and found, it is said, correct within $\pm$ 3 per cent., provided that the portion of the oil, which does not contain cineole, consists only of terpenes and sesquiterpenes. The error will be the smaller, the greater the contents of cineole, but it may rise up to 6 per cent. in the presence of alcohols and esters. Cocking obtains his tables by systematically determining the solidification points, on the one hand, of numerous mixtures of cineole and terebene, and, on the other hand, of mixtures of cineole and sesquiterpene (copaiba oil). Graphically represented the points obtained give two curves, the maximum difference between which will correspond to a cineole contents of 6 per cent. In the intermediate curve of the author the error limit would be reduced to three per cent.

In a later communication Cocking[4]) refutes the objections which Bennett and Salamon had raised against the cresineol method in favour of their phosphoric-acid method. The author emphasizes that only the presence of large amounts (33 per cent.) of foreign ketones, terpene alcohols and, above all, of esters could increase the errors of his method to 6.3 per cent., whilst the phosphoric-acid method would, for various reasons which he discusses in detail, give results, too low by 13 per cent. maximum. These statements confirm our own experience with the phosphoric-acid method, to the uselessness and unreliability of which we have frequently drawn attention[5]).

In a further communication on the eucalyptole determination Bennett and Salamon[6]) confirm on the strength of their own experiments that Cocking's cresol method admits of an approximate, rapid and easy estimation of the cineole in eucalyptus oil, provided that more than 45 per cent. of cineole be present in the oil. The freezing-point method of Kleber and W. v. Rechenberg[7]) seems, according to the experiments of these authors, to give uniform results; but they find it only convenient when the eucalyptole contents amounted to more than 70 per cent.

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[1]) *Berl. Berichte* **53** (1920), 2072. — [2]) Cf. *Report* April **1914**, 147. — [3]) *Perf. Record* **11** (1920), 281. — [4]) *Perfum. Record* **11** (1920), 363. — [5]) Cf. *Report* October **1907**, 47; October **1915**, 17; **1920**, 34. — [6]) *Perfum. Record* **12** (1921), 11. — [7]) See p. 23 of this *Report*.

Menthol.—We take the following statistics on the production, prices and exports of menthol and of oil of peppermint from Japan during the years 1919 to 1920 from an American report[1].

Year	Menthol			Oil of Peppermint		
	production tons	price s per lb.	total exports tons	production tons	price s per lb.	total exports tons
1909	—	7.35	60.35	—	4.7	—
1910	—	8.8	31.74	—	5.1	—
1911	—	15.5	66.97	—	6.4	41.16
1912	—	21.2	78.48	—	5.6	39.79
1913	—	19.3	137.26	—	6.1	75.55
1914	142.9	9.2	158.67	145.8	3.3	92.57
1915	223.9	8.5	188.76	257.0	2.6	75.80
1916	210.5	10.1	227.73	241.6	3.1	104.13
1917	252.8	10.0	147.92	254.2	2.8	68.26
1918	196.5	14.4	132.32	232.4	3.4	68.46
1919	147.3[2]	31.6	132.59	89.3[2]	7.2	85.95
1920	118.3[2]	43.0[3]	7.95[2]	118.3[2]	10.2[3]	11.36[3]

Musk, Artificial.—In an article on solid, artificial odoriferous substances W. H. Simmons[4] points out that the quality of artificial musk, coumarin and heliotropin had deteriorated in England since the war, partly because the raw materials had not been available in sufficient quantities, partly because the manufacture had been taken up by people not commanding the necessary experience. Whilst before the war the melting points were 109 to 113° for xylene musk and 36° for heliotropin, they were now mostly not higher than 105° or 35°. An ambrette-musk of a melting point between 60 and 90° would correspond to the requirements which were now made for an average post-war article.

Referring to this research by Simmons, W. E. Ellis[5] asserts on the strength of experiments of his own, that the melting point of 110 to 113° which von Baur gives for xylene musk cannot be correct. A pure preparation of Ellis, re-crystallised seven times from alcohol, had a constant melting point 107.9°, and another sample obtained from a first-class firm melted at 107°.

Nitrobenzene.—We cannot often enough emphasise the poisonous character and dangers of nitrobenzene. The following case will show very clearly how dangerous can be the effects even of very small quantities of essence dé Mirban. Linen which had freshly been stamped with a dye containing nitrobenzene caused, according to H. Ewer[6], poisoning in the cases of five babies, the symptoms being: blue discoloration of the skin, superficial respiration, irregular pulse, vomiting, and clonic convulsions. Bleeding had a good effect, inhalation of oxygen had no effect.

D. M. Donovan[7] reports several cases of nitrobenzene poisoning of adults. Thus sixteen people, then in military service, fell ill after wearing shoes dyed with nitro-

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[1] *United States Commercial Reports* of Febr. 3, 1921. — [2] Inofficial estimate. — [3] January to June 1920. — [4] *Perfum. Record* 11 (1920), 368. — [5] *Ibid.* 396. — [6] *Therap. Halbmonatsh.* 35 (1921), 62. *Berl. klin. Wochenschr.* No. 38, 1920; from *Pharm. Ztg.* 66 (1921), 72. — [7] *Journ. Americ. Med. Assoc.* 74 (1920), 1467; from *Therap. Halbmonatsh.* 34 (1920), 433.

benzene colours. Serious cases of poisoning were caused by alcohol which had been denatured with nitrobenzene. In one instance the patient died 45 minutes after arriving in the hospital, although at once treated with stimulants and oxygen. The author cautions against the practice of denaturing alcohol with nitrobenzene.

According to S. Hindse-Nielsen[1] a grave case of poisoning, caused by taking one tablespoonful of nitrobenzene (for abortive purposes), was cured by bleeding and infusion of one litre of citrate-blood.

Peru Balsam.—C. T. Bennett[2] has published contributions to the analysis of Peru balsam, based upon his experience and observations. Peru balsam is not a pure natural product, but is prepared by the searing of wounds of the trees, and undergoes in this procedure a change which is not always uniform. Moreover, the product was frequently adulterated with the secretions of other leaves, already in the process of gathering, either from ignorance or intentionally. It would hence be explicable why even authenticated samples frequently give discordant results in the analyses.

The balsam contains benzoic and cinnamic esters of the cinnamic and benzyl alcohols, free cinnamic acid, Peru resitannol esters of the cinnamic acid and benzoic acid and traces of vanillin and coumarin.

The estimation of the cinnamein contents is certainly valuable for the valuation of Peru balsam, but it is not by itself decisive. We have to consider that it is possible to increase the contents of cinnamein at will by adding artificial esters of benzoic acid. There is a striking contradiction between the requirements of the British and the American pharmacopœia. The former demands 57 per cent., the latter 50 to 56 per cent. of cinnamein. A balsam containing 56 and 57 per cent. would, therefore, not accord to either of the two pharmacopœias. According to Bennett the cinnamein contents of genuine balsam lies between 51 and 66 per cent. The test directions specified in the two pharmacopœias differ in their detail, but they give practically the same results.

Bennett gives the following constants for genuine balsams:—d_{15° 1.40 to 1.160; n_{D25° 1.5886 to 1.5952; n_{D25° of cinnamein 1.5750 to 1.5820; soluble in 10 vol. 92.3 per cent. alcohol with slight turbidity; sap. v. of cinnamein 229 to 257. He could not confirm Dieterich's iodine values, 22 to 26 for balsam, and 7.5 to 7.9 for cinnamein, but his figures, 40 to 43 for balsam, and 20 to 30 for cinnamein, agree with those of Jansen.

It is essential for the chloral hydrate test that the chloral hydrate be perfectly dry. That was first pointed out years ago by G. Fromme[3].

The presence of fatty oils in the balsam is best proved in the following way according to Delphin. The balsam is saponified with alcoholic caustic potash, and an aqueous solution of the fat as potash soap is prepared. When fat is present, it can easily be found by means of a solution of calcium chloride.

The colour reaction described by the American pharmacopœia for the determination of rosin and oil of turpentine is generally applicable according to Bennett, but a slight momentary green coloration must not be accepted as proving the presence of rosin. The author himself recommends the following reaction:—The extract of the balsam prepared with petroleum ether is shaken with the same volume of a one per cent. solution of copper acetate. In the presence of rosin the petroleum ether will assume a green colour.

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[1] *Ugeskrift f. laeger* 82 (1920), 1157; from *Therap. Halbmonatsh.* 35 (1921), 95. — [2] *Perfum. Record* 11 (1920), 131. — [3] Cf. *Report* October 1911, 114.

With respect the testing of Peru balsam we take the following notes from a paper by H. Wolff[1]. Of the various methods which the author studied testing with petroleum ether after Hager-Enz[2] gave the most uniform results. With pure balsam the ether remained perfectly clear, whilst separations appeared in artificial balsams or mixtures of genuine balsam with 20 to 30 per cent. of artificial balsam. On the other hand the ester test after Fromme[3] failed. The Herzog[4] zone test was only then found decisive, when the green colour did not appear. The nitric acid test after Fromme[3] was not always reliable either.

According to the experience of Wolff an adulteration of the balsam may therefore only be considered as established, when both the test with petroleum ether and the colour reaction indicate an addition, but not when only the colour reaction indicates this.

A Peru balsam examined by L. van Itallie[5] which had been adulterated with phthalic acid anhydride had the following constants:—d 1.146; acid v. 48.8; sap. v. 356; cinnamein 70 per cent.; sap. v. of the cinnamein 382. The ester was easily identified by the fluorescein reaction with resorcinol and sulphuric acid. Another, so-called synthetical Peru balsam had the constants:—Acid v. 48.1; sap. v. 220.4; cinnamein 64 per cent.; sap. v. of the cinnamein 254; n of cinnamein 1.5682. Although the quantitative analysis yielded normal figures, qualitative tests suggested an artificial product prepared with benzyl benzoate.

Pollantin.—The proteins of various kinds of pollen play, as is well-known, an important part in the hay-fever trouble. Apart from the pollens of grasses and cereals, which are significant for the disease in Europe, there are the pollens of a series of American *Ambrosia* and *Solidago* species, to which the excitation of the disease is described. As regards the protein-bodies of the ambrosia-pollen, Fr. W. Heyl, who had already published several reseaches on this problem[6], has communicated a new paper in conjunction with H. H. Hopkins[7], in which they give expression to somewhat novel views.

In the treatment and preparation of drugs, they point out, two methods should be distinguished. The first is mainly concerned with chemical attack and aims at final pure products or at crystalline substances. The second, conservative method is characterised by the application of the more simple pharmaceutical modes of working and prefers the preparation of the so-called galenical preparations or extracts.

The ragweed pollens (ambrosia-pollen) belong, according to the authors, to the drugs which should be treated according to the second method. For our imperfect knowledge of their compositions does not justify any chemical decomposition of the drugs into "pure" substances, even it we acknowledge that the albumin reaction of the proteins claims the main interest and assume that the hay-fever toxin from the pollen of the grasses approaches, as a toxalbumin, the albuminous poisons, ricin, abrin and crotin, and produces in the animal body a specific antitoxin. For all that we need not make the same assumption for the ragweed pollen.

In an investigation of the ragweed pollen Kammann[8] has proved that the pollen-poison, extracted by means of water from the pollen, does not only resist the attacks of the pollen proteases (ferments destroying albuminoids), which are likewise present

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[1] *Pharm. Ztg.* **66** (1921), 38. — [2] *Süddeutsche Apotheker Ztg.* **1913**, 73. Cf. *Report* April **1914**, 108. — [3] *Berichte* of Caesar and Loretz **1913**, 17. — [4] *Riedel-Archiv* **1914**, 65. — [5] *Pharm. Weekblad* **1920**, No. 45, 1383. Reprint was kindly sent to us. — [6] Cf. *Report* **1918**, 65; **1920**, 75. — [7] *Journ. Americ. chem. Soc.* **42** (1920), 1738. — [8] *Biochem. Zeitschr.* **46** (1912), 151; *Report* April **1913**, 118.

in the extracts, but is even a hundred times more efficient. On the other hand he states that treatment of the poison with artificial trypsin leads to the complete loss of the toxic character. How is this contradiction to be explained? Further, how can it be explained, when Kammann establishes that the poisonous efficiency diminishes, in the precipitation and coagulation of the albumin fraction by means of alcohol, with the prolonged action of the precipitant, whilst it was maintained by others that the poison was thermostable. According to the authors Kammann has been misled by the idea to prepare from the pollen a non-nitrogenous (and, therefore, free of albumin) thermostable poisonous component, similarly to what Keyes and Faust have done with the cobra poison, when they prepared a so-called ophiotoxin from the cobra poison; this toxin the latter consider to represent a compound of the salt or ester type with the albumin fraction, which is precipitated by coagulation together with the fraction and can be liberated again by means of chemical reagents.

On the whole the authors deem it advisable to make use only of *native pollen extracts* which they consider to be more stable and more active than any isolated and purified special fractions (Galenical principle).

The analytical data concerning the distribution of nitrogen through the different degradation-products of the pollen-proteins are in this connection of lesser interest.

Kammann replies to this paper by Heyl and Hopkins, reserving a more detailed critical answer in the technical press, in the following way:—

In my paper on "The Rye-Pollen"[1]) I have shown that the rye-pollen consists of a manifold mixture of inorganic and organic substances which, to a large degree, can pass into water or into a diluted solution of salt, either in the dissolved, or in a colloidal condition. Concerned are a series of inorganic salts, oils, fats and waxes, ferments, carbohydrates and protein-bodies of pollen; the latter can further be separated, again by displacement-reactions, *i. e.,* not by chemical attack, into three main fractions, the euglobulins, pseudoglobulins, and the albumins. According to unpublished researches the pollens of the solidago and ragweed are equally complex. Would we not be justified then to abandon the galenical principle, which is admittedly useful and applicable under certain definite conditions, but which here deals in an almost brutal way with bewildering mixtures of substances, the single actions of which are unknown and the total, combined effects of which can hardly be foreseen in all their consequences? With a mixture of substances, moreover, 90 per cent. of which have not the slightest share in the desired immunisation and cure, which perhaps they do not allow to develop, if they do not actually inhibit them?

I have in one case found direct experimental proof of an antagonistic effect of this kind even in the starch contents of the pollen. In addition to the partial poison proper, which causes the hay-fever, there is in this hay-fever poison a second poisonous component of hæmolytic properties. The hæmolytic activity (dissolution of blood corpuscles) is less marked, or not observable at all, when the starch present in the pollen of grasses is left in the extract. This is a typical example of a colloidal protection, where the starch acting as protective colloid masks or inhibits any hæmolytic action. When the carbohydrates are removed by the fermentative action, I have indicated, the hæmolytic component becomes again active. The same is true with regard to the starch contents for the partial poison causing the hay-fever; after suitable biological removal of the starch the poison shows for that very reason its effect magnified a hundredfold.

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[1]) *Beiträge zur chem. Physiologie und Pathologie,* vol. V, No. 7 and 8.

Is there any more convincing proof for justifying our giving up the galenical principle which, it is true, does not require much trouble, nor ingenuity, and for our having recourse to the more conservative physical and biological methods, which will lead to the aim desired by laborious and extensive studies, if carried out with the necessary knowledge of the facts?

Which then are the successes aimed at?

In the first instance, it is possible to prepare a poison which, in its efficiency, exceeds the simple extracts and poisons so far known more than a hundred times without in the least impairing its specific character. Secondly, the living organism responds to the incorporation of the poison by so much increased counter-effects that we no longer find thirty to forty antitoxin units per serum unit, as before, but three hundred and more.

Are the methods of physical chemistry and applied biology used really conservative?

The answer will be easy to anybody who understands such methods, and who has thoroughly studied the paper, I have spoken of, on "Further Studies concerning Pollen Toxin". Contrary to the views of Heyl and Hopkins, I state there expressly that, so far, such methods had mainly been employed, for the preparation of antigens, as were customary in chemistry and cognate sciences, that these methods could only lead to entirely-incomplete explications owing to the instability of the material worked with, and that the more refined biological methods should replace the chemical methods of separation which fail in these cases.

My researches are based upon biological methods and upon physical modes of working.

If now Heyl and Hopkins find a contradiction in my statements by pointing, on the one hand, to a non-deterioration of the hay-fever poison by the pollen proteases, on the other hand, to a complete destruction of the poison by an artifical protease, the trypsin, this only shows that the fermentative methods and their effects are not sufficiently at their command, if they create such contrasts.

There are a series of proteases with tryptic effects which all differ as to their specific power of attacking substrates, their effective temperatures and their efficiency. The one ferment attacks only a certain protein, leaving others uninfluenced; another ferment has its temperature optimum at 37° C. and becomes more or less inactive at other temperatures; a third destroys the bricks of albuminoids to a certain extent, and so on.

The trypsin proper now has the strongest known tryptic effect. It develops its optimum force at blood temperature, and in alkaline solution. We cannot be surprised, therefore, that it should in alkaline solution at a temperature of 37° C., given sufficient time of action, also attack the components of the pollen toxalbumin causing the hay-fever. Heyl and Hopkins, however, are again in error when they quote from my paper on "the Investigation of Rye Pollen and of the Hay-Fever Poison in it" *(Beiträge zur chem. Physiol. u. Pathologie*, vol. V, N°. 7 and 8) a remark to the effect that the treatment with trypsin would lead to a loss of efficiency. The final paragraph 4 of my paper states expressly that enzymes like pepsin and trypsin can *not* completely destroy the poison.

Even if, however, a complete destruction by trypsin were possible, this action cannot be compared at all to the fermentative influences of the pollen proteases. The latter, it is true, must be counted among the tryptic ferments, but they do not possess anything like the hydrolysing power of the trypsin and develop these weaker effects only in alkaline solution and at the optimum temperature of 30 to 40° C.

My direction as to the preparation of the intense pollen-toxin, on the contrary, deals with the action of *single* pollen proteases upon the pollen albuminoids in *neutra* media and in an ice-box at a temperature of 4 to 6° C. Its only purpose is to separate the ballast-albuminoids, recognised to be ineffective, from the poisonous component proper. That this separation has been successful beyond expectation is shown by what I have said above concerning the increased specific poisonous activity and intensified counter-reactions by the living organism thus treated. The question whether the poisonous effect is to be ascribed to some protein, in this case the pollen albumin, or whether it is only adherent to it, remains for the present entirely open.

The contradiction which Heyl and Hopkins have construed into my statements must therefore fall.

The second objection raised by Heyl and Hopkins does not fare any better. They maintain that according to my statements the hay-fever poison would lose its efficiency by being precipitated and by standing for some time in alcohol, but would not be impaired by heating, because it was thermostable. The authors must have been misled by the idea that a coagulation of albuminoids by alcohol and by heat is the same thing, and that the two processes should be accompanied by the same effect. Let us examine my statements.

In my paper on "Further Studies concerning Pollen-Toxin" I state that the albumins are precipitated from their aqueous solution by eight to ten-fold the bulk of alcohol, and that it is advisable to shorten this treatment with alcohol, *although any considerable detriment to the pollen-toxin would not result.* How do Heyl and Hopkins come to assert that treatment with alcohol should result in a loss of efficiency?

If I have said in my paper on the "Study of Rye Pollen, &c." that the hay-fever poison is thermostable, that, it will easily be understood, is to be taken conditionally. The published data of my heat experiments demonstrate that temperatures of 70° C. and more already diminish the toxicity to about one-quarter of its original value.

Coagulation by alcohol and coagulation by heat are, moreover, so different matters that we must not conclude equal final effects from the equal external appearance of the coagulates. Once more the authors cannot be spared the reproach of not having proceeded with the necessary knowledge of the facts.

The statements by Heyl and Hopkins have not only not been able to convince me of the utility of the galenical principle, which they praise, in cases of the complex problems of the various hay-fever poisons including the ragweed poison, but they can only confirm the belief in more penetrating and thorough methods of research.

Storax.—The literature distinguishes, in addition to Oriental storax balsams, two storax species of American origin:—American storax and Honduras balsam, also known as white Peru balsam¹). The mother plant of the American storax is the tree *Liquidambar styracifluum,* L., which grows in the South East of the United States and in Central America. According to A. Tschirch²) the Honduras balsam is also obtained from a species of *Liquidambar.* In each of the two oils, which are obtained by steam distillation from these balsams, the chemical investigation has revealed cinnamyl alcohol and phenylpropyl alcohol and esters of the cinnamic acid and these alcohols. In the oil from the so-called American storax there has also been found styrene and a small quantity of an aldehyde which smells of vanillin.

The presumption appears justified that the two kinds, which are described under different names, really represent the same commercial product which originates from Honduras. As we mentioned in our last *Report* but one³), the mountains of this country

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¹) Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. II, p. 542, 543. — ²) *Die Harze und die Harzbehälter,* 2nd ed., vol. I, p. 322. Leipzig **1906**. — ³) *Report* **1919**, 72.

are covered with extensive forests of that tree *Liquidambar styracifluum,* L., which has been exploited by the natives for centuries.

The centre of the storax-balsam districts is now in the environs of the town of Santa Bárbara. From there the storax is exported under the name of *Liquidambar* or simply as balsam *via* the port of Puerto Cortés.

A consignment of storax balsam from Honduras which we recently received gave the following constants after drying and filtration:—d_{15° 1.0977; $\alpha_D + 11^\circ$; n_{D20° 1.59485; acid v. 33.6; ester v. 139. At ordinary temperature it forms a clear, amber-yellow, somewhat viscid mass. When the balsam was boiled with aqueous caustic potash, an oil of pleasant odour, dark colour and the following constants passed over:—d_{15° 1.002; $\alpha_D + 1^\circ 10'$; n_{D20° 1.54429; acid v. 1.8; ester v. 8.4; ester v. after acetyl. 243.6. The oil distilled in a vacuum at 4 mm. between 23 and 111°.

The acetylation shows that the oil consists essentially of alcoholic constituents. We were, however, able to isolate styrene of a b. p. of 144 to 146° from the lower-boiling fractions which, brominated in ethereal solution, gave the dibromide melting at 74°.

In the fraction of the oil boiling between 118 and 121° (5 mm.) solidified a compound which consisted of cinnamic alcohol melting at 33°.

This alcohol was also found in large quantities in the fractions boiling between 95 and 118° at 5 mm., in addition to phenylpropyl alcohol.

In order to prepare the latter alcohol in the pure state, these fractions were boiled with formic acid for one quarter of an hour, and the phenylpropyl formate thus obtained was separated by distillation from the resinified cinnamic alcohol. From the formate, pure phenylpropyl alcohol of d_{15° 1.0027 could be isolated by saponification; by oxidation with chromic acid in glacial acetic acid hydrocinnamic acid melting between 48 and 49° was isolated. By heating the ammonia salt up to 230° in a sealed tube the amide of hydrocinnamic acid, melting at 104°, was produced. Treatment of the phenylpropyl alcohol with phenyl*iso*cyanate yielded a phenylurethane, melting point 47°, from ligroin. The saponification-lye of the storax balsam contained cinnamic acid, m. p. 133°; benzoic acid could not be found in determinable quantities.

The result of the investigation was, therefore, that the essential from Honduras balsam contains the constituents, which were already known in the oil of American storax, including styrene; the latter had not yet been proved to be present in Honduras balsam[1]).

By working up a larger bulk of Honduras balsam it may be possible to demonstrate also the presence of the aldehyde (vanillin) which occurs in American balsam in small proportions.

Since now the essential oils of American balsam and of Honduras balsam show substantially the same composition, there is no cause to maintain a distinction between the two species. We may on the contrary assume that all the American storax balsams, so far studied, represent one and the same product of *Liquidambar styraciflium,* L., on the formation of which we have already reported[2]).

Thymol.—In our *Report* of last year we mentioned on page 76 that, according to an American patent, thymol may be prepared from 2-aminocymene. The *thymol synthesis* from cymene, which M. Phillips and H. D. Gibbs[3]) describe, is based on a similar method. In general the phenols are prepared from the corresponding hydrocarbons by decomposing the diazo-compound, especially the sulphonate, with boiling water, and by fusing the sulphonic acid produced with potassium hydroxide. This

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[1]) A. Hellström, *Arch. der Pharm.* **243** (1905), 237. — [2]) *Report* **1919**, 72. — [3]) *Journ. ind. eng. Chem.* **12** (1920), 733.

simple method is not directly applicable for the thymol synthesis, since in the sulphonation or nitration of the *p*-cymene the substituted radicle always takes the *o*-position with respect to the methyl group. The authors succeeded by the following indirect method:—They nitrated *p*-cymene, reduced the 2-nitrocymene produced to 2-aminocymene, sulphonated the latter by the baking process[1], used in the preparation of sulphanilic acid, diazotised the 2-aminocymene-3- and -5-sulphonic acids obtained, reduced the product of the reaction to the sulphonic acid of 3-cymene (only the latter is produced) and obtained finally thymol-sodium, by means of fusing with sodium hydroxide, and further thymol itself.

The raw material in this reaction was the *p*-cymene obtained in the manufacture of the sulphite spruce pulp (m. p. 174 to 175°, ordinary pressure). By this method the authors obtained 32 per cent. of the theoretically-possible yield of aminocymenesulphonic acid and 40 per cent. (calculated as acid) of the theoretical quantity of pure thymol (phenylurethane, m. p. 107°).

As regards details it should be emphasised that the preparation of 3-cymene sulphonic acid from 2-aminocymene-3-sulphonic acid was successful by the slightly-modified Widman process[2] (addition of powdered copper in reducing the diazo-compound). Without this addition, which may also consist of zinc dust, sodium ethylate, sodium hydroxide, potassium carbonate or sodium methylate, the reduction of the diazo-compound in boiling alcohol would yield an ethoxy-derivative[3].

In order to determine the thymol in the oil of *Mosla japonica*, Maxim., T. Kariyone and A. Katsumi[4] recommend a method which essentially corresponds to the method of Kremers and Schreiner[5]. The authors precipitate, from the alkaline solution in phenol, the thymol by means of 15 per cent. hydrochloric acid, re-dissolve it in alkali and titrate it in the known manner by means of iodine and sodium thiosulphate. The errors of this method are said not to amount to more than 2 per cent., provided that the total contents of phenols in the oil, as in the *Mosla japonica*, do not exceed 9 per cent.

We have already reported at some length[6] on the cultivation in Florida of *Monarda punctata* which is known in America as horse mint. According to an article by G. A. Russell[7], which is essentially based upon the statements of Hood[6], the cultivation of this plant has, even in the last years, not brought any better profits. In the year 1917 the harvest was much impaired by diseases; in 1918 and 1919 it was not possible to manure the enlarged plantations sufficiently.

In order to increase the yield of oil the author recommends to re-distil the distillation water which still contains 9.5 per cent. of the total oil, consisting mainly of portions very rich in phenols (above all thymol). The phenol contents of the monarda oils which were obtained in the years 1914—1919 in Satsuma Heights, Putnam county, Florida, and in Orlando, Florida, amounted to 65.3 to 70 per cent.

The publication of an article on piperitone by Smith and Penfold—concerning the preparation of thymol, menthol and menthone (compare page 23 of this *Report*)—induced a London firm to offer larger quantities of peppermint ketone for the preparation of thymol at a price of 4/6d. to thirty chemical factories in England. Thymol being

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[1] The acid sulphate of the sulphanilic acid is baked in an oven to facilitate the conversion into sulphanilic acid. *Zeitschr. f. angew. Chem.* 9 (1896), I. 685. — [2] *Berl. Berichte* **15** (1882), 166. — [3] Cf. *Berl. Berichte* 18 (1885), 65. — [4] *Yakugakuzasshi* No. 457 (1920); from *Journ. de Pharm. et Chim.* VII. **23** (1921), 41. — [5] Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 594. — [6] Cf. *Report* **1916**, 78; **1917**, 100. — [7] *Americ. Perfumer* **15** (1920), 365.

then paid in London 45 to 40/- per lb. a yield of 25 per cent. of thymol, realisable in the preparation by the method of Smith and Penfold (by the oxidation of piperitone, ferric chloride and glacial acetic acid) would promise a good clear profit (something like 16/- per lb. of thymol)[1].

L. Thimm[2] recommends thymol palmitate for the disinfection of the intestines, especially in cases of dysentery. The saponification of the ester takes place in the intestines, and the thymol liberated acts without any poisonous effects, except in the case of to very sensitive persons. Similarly thymol palmitate has been recommended by F. Munck[3] as a remedy against trichinosis.

When the trichinæ have already penetrated into the muscles Kahn[4] used subcutaneous or intramuscular injections of a six per cent. solution of thymol in olive oil with success.

According to E. Edens[5] the continued application of even very small quantities of thymol may injure the thyroid gland in sensitive persons and lead to their losing flesh.

An injection anæsthetic called "novorenan" which is recommended by Müller-Stade[6] has the following composition: — novocaine 0.01 g., suprarenin hydrochloride (1 = 1000) one drop, thymol 0.001 g., physiological sodium chloride solution ad 1 cc.

Three per cent. thymol spirit (prepared with 60 per cent. alcohol) is according to the experience of C. Hirsch[7] a good and harmless skin disinfectant.

The ethyl and methyl ethers of thymol are with intravenous injection in 10 per cent. solution much less poisonous than thymol itself. On the other hand, thymol sodium is more poisonous even than thymol[8].

As regards the poisonous effects of large quantities of thymol, cf. *Report* **1918**, p. 70.

Vanillin. — It is well known that vanillin, or substances which yield vanillin by hydrolysis, are frequent in nature and occur not only in the pods of vanilla, *e. g.*, in the flowers of *Nigritella suaveolens*, Koch[9] and other, especially exotic orchids, but also in the seeds of *Lupinus albus*, L.[10], in ilex leaves[11], in potato flowers[12] and in cork[13].

Recently A. Büchel[14] has drawn attention to the fact that vanillin is also contained in the flowers of the *Scorzonera*[15] of our gardens. The smell of vanillin was particularly distinct when the sun was shining on the flowers after rain.

Since the pimento leaf oil coming from Jamaica contains 89 per cent. of eugenol according to the Imperial Institute of London (cf. page 35 of this *Report*), the Government[16] were intending to start a vanillin industry in that country. Much importance is attached to the fact observed by Campbell that the fermentation process of the leaves transforms eugenol spontaneously into the *iso*-compound, an intermediate product

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[1] *Perfum. Record* **12** (1921), 42. — [2] *Deutsche med. Wochenschr.* No. **26** (1918), 716. — [3] *Med. Klinik* No. **15** (1917), 429. — [4] *New-York Medical Journal* of 16. VI. **1917**, 1137. — [5] *Med. Klinik* No. **30** (1917), 807. — [6] *Deutsche zahnärztliche Wochenschr.* No. **21** (1917), 249. — [7] *Zentralbl. f. Chirurgie* No. **3** (1918), 35. The references 2 to 7 are taken from E. Merck's *Jahresbericht* **31** to **32** (1917 to 1918), 364 and 501. — [8] *Compt. rend. soc. de biologie* **83** (1920), 1149; from *Chem. Zentralbl.* **1920**, III. 524. — [9] *Berl. Berichte* **27** (1894), 3409. — [10] *Chem. Zentralbl.* **1888**, I. 377. — [11] *Arbeiten a. d. Kais. Gesundheitsamt* **15** (1898), 171. — [12] v. Lippmann, *Berl. Berichte* **52** (1919), 905; *Report* **1919**, 76. — [13] *Pharm. Zentralh.* **39** (1898), 685. — [14] *Apotheker Ztg.* **35** (1920), 237. — [15] *Scorzonera hispanica*, L., cultivated for the sake of their roots, are probably meant. — [16] *Chemist and Druggist* **93** (1920), 1253. *Americ. Perfumer* **15** (1920), 244.

in the conversion into vanillin. The view is entertained that the utilisation of this observation would render the manufacture of vanillin much less expensive. We shall have to see whether the success will correspond to the great expectations which English journals place upon this news.

According to an American communication[1]) a hundred thousand pounds of pimento leaf oil might be obtained *per annum* in Jamaica from waste material.

We have in the last years repeatedly observed an adulteration of preparations like coumarin, heliotropin and vanillin by the addition of inorganic salts. We have already pointed out on former occasions[2]) that such falsifications are rather clumsy, since the inorganic salts can easily be recognised by their insolubility in alcohol and ether, and that they would not long remain obscure even to the consumer, because the aromatic substances in question are very frequently used in alcoholic solutions. The thing seems to pay in spite of that, since we meet over and over again from time to time with such additions. Recently we received a sample each of vanillin and coumarin in our laboratory for examination in which we detected the mentioned adulterations. To make a change magnesium sulphate had been used in this instance; formerly it was sodium sulphate. When we treated the two samples with ether, the magnesium sulphate remained quantitatively on the filter and could be detected by means of its properties. The proportion amounted to 18.6 per cent. in the vanillin, and to 15 per cent. in the coumarin. In both cases this was the only adulteration applied; for after removal of the magnesium sulphate, both the samples showed the correct melting point, vanillin 82° and coumarin 70°.

The vanillin had been sent to us from Italy, the coumarin from Sweden.

H. Schellbach and Fr. Bodinus have continued their investigation[3]) of the volatility of vanillin in sugar and flour mixtures[4]). The tables of their experimental data show that vanillin volatilises more easily from mixtures with crystalline sugar than from mixtures with powdered dust sugar. The loss of vanillin is much influenced by the way in which the mixtures are stored. To diminish the loss, the mixture should be kept in cool and relatively damp places.

Since their results agreed neither with the statements of Sprinkmeyer and Grünert, nor with their own previous results, the authors conclude that not only the mode of packing, but also the mode of preparation and the purity of the vanillin are of influence with respect to the volatility.

The purity of the vanillin (*e. g.*, the presence or absence of bourbonal [ethylprotocatechuic aldehyde]) could not always be established with absolute certainty by the melting point determination.

The examination of mixtures of vanillin and flour required particular attention, because the usual method (extraction of the sample with anhydrous ether) failed in this case. The authors believe that a union, although loose, exists between vanillin and the starch molecule, which is only imperfectly influenced by ether. The original paper describes in detail how to avoid experimental errors.

As regards the solubility of vanillin in water and glycerin, confer page 88 of this *Report*.

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[1]) *United States Com. Rep.* of 1. XI. 1920. From *Journ. Soc. chem. Ind.* **40** (1921), R. 13. — [2]) *Report* **1918**, 72. — [3]) Cf. *Report* **1920**, 77. — [4]) *Zeitschr. Untersuch. d. Nahrungs- u. Genussm.* **40** (1920), 34.

Notes on Scientific Research in the Domain of the Terpenes and Essential Oils.

General.

D. Bernabé Dorronsoro has published an extensive memoir[1]) on the *essential oils obtained from the Spanish Flora.* The author discusses the chemical constituents of the oils, explains the known physical and chemical methods of investigation and describes finally the separate essential oils, giving details of his own results.

The *oil of turpentine* forms an important export article of Spain. The company *Union resinera española* controlled in the year 1910 54037 hectares of pine forests and supplied in that year 4728 tons of oil of turpentine. As the oil of turpentine destined for export is mainly obtained in the north of Spain, from *Pinus pinaster,* Sol. (*Pinus maritima,* Poir.), Spanish and French oils used frequently to be considered identical. Dorronsoro does not regard this as quite correct, without giving further reasons for his assertion.

In the second instance *Pinus Laricio,* Poir. *(pino negral)* and *Pinus halepensis,* Mill. *(pino carasco)* are of importance for the preparation of Spanish oil of turpentine.

The oils from *Pinus pinaster,* hailing from the provinces of Avila, Cáceres and Castellon had on average the following properties: — d_{15° 0.8674 to 0.8729; $[\alpha]_D$ — 28° 44′ to — 32° 3′; n_D 1.4705 to 1.4717; soluble in 5.5 to 7.5 vol. of 90 per cent. alcohol and in 21 to 25 vol. of 80 per cent. alcohol. In the distillation 68.3 to 78.7 per cent. passed over between 152 and 157° (700 to 710 mm.).

The oil of the *Pinus Laricio,* Poir., growing in Cuenza, had the following constants: — d_{15° 0.8648; $[\alpha]_{D20^\circ}$ — 25° 14′; n_{D20° 1.4691; soluble in 22 vol. 80 per cent. alcohol and in 7.5 vol. 90 per cent. alcohol; acid v. 1.22 (corresponding to 0.715 per cent. of colophony); 67.45 per cent. boiled in a Ladenburg flask (715 mm.) between 153 to 160°. These numbers are in pretty fair agreement with the constants[2]) which we found in an Austrian oil of turpentine (*Pinus Laricio* var. *β austriaca,* Endl.).

The *Pinus halepensis,* Mill., which is common also in Greece and thrives in southern and eastern Spain, yielded oils of the following constants: — d_{15° 0.8721 to 0.8808; $[\alpha]_D$ + 0° 50′ to + 4° 15′ n_D 1.4688 to 1.4716; soluble in 6.4 to 7.5 vol. 90 per cent. alcohol; acid v. 0.64 to 1.99 (corresponding to colophony contents of 0.375 to 0.97 per cent.); boiling in Ladenburg flask (705 mm.) 150 to 155° (39 per cent.) and 152° (49.03 per cent.). Attempts to prepare sodium nopinate had no success; in its place he obtained considerable quantities of oxalic acid. The oxidation with permanganate without alkali yielded pinic acid. In addition to *β*- and *α*-pinene there is probably present in the oil another, so far unknown pinene. Unexplained is further the fact that Fernandez[2]), investigating the same Spanish oil years ago, found quite different constants.

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[1]) *Estudio Quimico de Esencias naturales españolas. Memorias de la Real Academia de Ciencias Exactas, Fisicas y Naturales de Madrid* 29, 1919. — [2]) Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. II, p. 75.

From the sprouts of *Pinus halepensis*, Mill. Dorronsoro obtained an oil, yellowish-green, of agreeable odour and of the following properties:—$d_{19^\circ}^{19^\circ}$ 0.872; α_{D17° — 3° 30′; $[\alpha]_{D17^\circ}$ —4.013°; acid v. 0.8; ester v. 31.9; ester v. after acetyl. 51.2; ester 11.165 per cent. (calculated as $C_{10}H_{17}O \cdot CO \cdot CH_3$), free alcohol 6.21 per cent., combined alcohol 8.78 per cent., total alcohol ($C_{10}H_{18}O$) 14.64 per cent. Soluble in 25 vol. 90 per cent. alcohol. Fractions at 710 mm.:—168 to 174°, 18.75 per cent.; 174 to 180°, 36.60 per cent.; 180 to 245°, 14.71 per cent.; 245 to 275°, 19.40 per cent.; 275 to 300°, 5.80 per cent. These numbers differ strongly from the constants which Belloni[1]) found in a French Aleppo pine oil.

In addition to much pinene the oil contained probably dipentene to judge by the melting point (of 125°) of the tetrabromide. Ethylfenchyl alcohol and its acetate were probably likewise present, though they could not be identified with certainty.

The *Cypress Oil*, obtained from Carcagente (Valencia) out of *Cupressus sempervirens*, had the following properties:—d_{15° 0.8942; α_D $+25^\circ\,20'$; n_{D20° 1.4810; acid v. 0.6; ester v. 23.2 (corresponding to 8.12 per cent. of terpinylacetate), ester v. after acetyl. 44.06 (corresponding to 12.12 per cent. of total alcohol). Soluble in 6.4 vol. 90 per cent. alcohol. Behaviour in Ladenburg flask:—(715 mm.) 145 to 155°, 7.68 per cent.; 155 to 156°, 11.07 per cent.; 156 to 158°, 14.63 per cent.; 158 to 162°, 20.65 per cent.; 162 to 190°, 24.95 per cent.; 190 to 200°, 7.65 per cent.; residue 13.37 per cent. The oil contained ample proportions of cedrol.

A *Juniper Berry Oil* with the following constants differed markedly from oils of other countries:—d_{15° 0.9093; α_D — 4° 40′; n_D 1.4868; acid v. 4.0; ester v. 19.82; soluble in 0.5 vol. and miscible without turbidity with 4.5 and more vol. 90 per cent. alcohol; soluble in 15 vol. 80 per cent. alcohol.

On the other hand, the properties of the *Savin Oil*, from Sevilla, agreed fairly well with those of genuine, non-Spanish savin oils. d_{15° 0.9075; α_D $+53^\circ\,38'$; n_D 1.4760; acid v. 2.51 (corresponding to 0.27 per cent. of acetic acid); ester v. 107.98 (corresponding to 37.40 per cent. of sabinyl acetate [= 29.3 per cent. of sabinol!]; ester v. after acetyl. 123.48 (corresponding to 4.45 per cent. of free and 36.87 per cent. of total sabinol). In the distillation in a Ladenburg flask (710 mm.) 18 per cent. of the oil passed below 175°, and 44 per cent. below 193°. The constants of the nine fractions of oil between 160 and 255° indicated that sabinene, sabinol and its esters and cadinene were present.

The production of *Agrumen Oils*, formerly not important in Spain, has only in recent time undergone development. Three samples of an expressed lemon oil from Sevilla, Valencia and Malaga had the following properties:—$d_{20^\circ}^{20^\circ}$ 0.8494 to 0.8524; α_{D20° $+56^\circ\,16'$ to $59^\circ\,15'$; α_D of the first tenth of the distillate $+54^\circ\,0'$ to $+55^\circ\,44'$; n_{D20° 1.4732 to 1.4746; evaporation residue 3.45 to 5.90 per cent.; citral contents (hydroxylamine method) 2.40 to 4.01 per cent.

Three distilled *Lemon Oils*, from Alora, Cartama and Pizarra (province of Malaga) gave the constants —d_{20° 0.8463 to 0.8486; α_{D20° $+64^\circ\,44'$ to $+68^\circ\,0'$; n_{D20° 1.4732 to 1.4734; evaporation residue 1.7 to 3.3 per cent.; citral (hydroxylamine method) 1.80 to 2.87 per cent. The author accounts for the generally low percentage of citral by the fact that the oils had been obtained only from quite ripe fruit; in the latter the ratio of terpene to citral is displaced to the disadvantage of the aldehyde.

A *Bitter Orange Peel Oil*, which had been supplied by Sevilla firm of good repute under the designation "extra", proved to be strongly adulterated:—d_{20° 0.8852; α_{D20° $+80^\circ\,30'$;

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[1]) Cf. *Report* April **1906**, 57.

α_{D20° of the first tenth of the distillate + 93° 28′; n_{D20° 1.4799; acid v. 3.1; ester v. 41.32; ester v. after acetyl. 78.90; evaporation residue 15.6 per cent.

Three expressed *Sweet Orange Peel Oils*[1]) from Sevilla, Carcagente and Malaga and a rectified product from Carcagente had the following constants:—d_{15° 0.8542 to 0.8568 and 0.8532; α_{D20° + 92° to + 93° 6′ and + 97° 25′; α_{D20° of the first tenth of the distillate + 97° 36′ to + 99° 36′ and + 98° 20′; n_{D20° 1.4753 to 1.4782 and 1.4736; acid v. 3.0 to 7.2 and 1.6; ester v. 10.76 to 17.82 and 2.2; ester v. after acetyl. 23.44 to 33.94 and 18.02; evaporation residue 6.6 to 12.44 and 2.55 per cent.; citral[2]) (bisulphite method) 1 per cent. Of the three expressed samples two were pale-yellow and one contained an orange-red colouring matter which was precipitated by the addition of 90 per cent. alcohol. This, undoubtedly genuine oil from Carcagente was soluble in 5 vol. 95 per cent. alcohol and in 13.5 vol. 90 per cent. alcohol. In the distillation in the Ladenburg flask 70.75 per cent. passed over between 170 and 172°. There were, therefore, present about 70 per cent. of pure *d*-limonene. The semi-solid distillation residue (12.87 per cent.) consisted, according to Dorronsoro, of citral[2]). The colouring matter and an ester in the residue could not be identified so far.

The three following products, one each coming from Carcagente and Sevilla, and one from Carcagente (rectified), are typical examples of genuine Spanish *Mandarin Oils*. Colour:—yellow, reddish or almost colourless with a strong blue-violet fluorescence; d_{20° 0.854, 0.8541, 0.8536; α_{D20° + 73° 4′; + 73° 0′; + 67° 43′; $[\alpha]_D$ of the first half of the distillate + 80° 30′; + 74° 50′; + 70° 50′; α_D of the remainder + 66° 10′; + 68° 56′; + 64° 14′; n_{D20° 1.4775, 1.4753, 1.4773; evaporation residue 7.95 per cent., 3.88 per cent., 2.6 per cent.; acid v. 4.15, 2.4, 1.9; ester v. 9.97, 9.84, 9.0; ester v. after acetyl. 17.34, 20.3, 14.28; soluble in 2 vol. 95 per cent. alcohol, in 14 vol., 12 vol., 9 vol. 90 per cent. alcohol; citral[3]) (hydroxylamine method) 2.28 per cent., 1.07 per cent., 1 per cent. (bisulphite method) 2 per cent. Of the expressed oils (Carcagente) 9 per cent. distilled in a Ladenburg flask between 165 and 170°, and 76.85 per cent. between 170 and 180°. The oil consisted, therefore, chiefly of *d*-limonene. The last fractions contained 3.5 per cent. of esters (calculated as acetate of an alcohol $C_{10}H_{18}O$) which were decomposed by heat.

Two *Petitgrain Oils* from Sevilla were greenish-yellow, transparent and faintly acid liquids which were soluble in any proportion of 90 per cent. alcohol:—d_{15° 0.8818 and 0.8845; α_{D20° + 6° 24′ and + 6° 48′; n_{D20° 1.4662 and 1.4661; soluble in 2 vol. and in 1.25 vol. 80 per cent. alcohol; acid v. 3.07 and 4.53; ester v. 72.46 and 80.37 (corresponding to 25.36 per cent. and 28.13 per cent. of ester [linalyl acetate]); ester v. after acetyl. 180.36 and 182.42 (corresponding to 57.32 per cent. and 58.08 per cent. of total alcohol [$C_{10}H_{18}O$]) and to 32.24 per cent. and 30.38 per cent. of free alcohol.

Of two *Bergamot Oils* from Sevilla and one from Valencia, two were found adulterated. The genuine product, styled "extra", yet not a first-class oil, from Sevilla had the following constants:—d_{15° 0.8812; α_{D20° + 16° 36′; n_{D20° 1.4660; soluble in 0.25 vol. 90 per cent. alcohol; acid v. 3.77; ester v. 105.47 (corresponding to a linalyl acetate content of 36.92 per cent.); ester v. after acetyl. 154.22; total alcohol 48.50 per cent., free alcohol 13.90 per cent.; evaporation residue 5.40 per cent.

Two genuine *Orange Blossom Oils* from Sevilla ("Neroli Bigarade extra" and "Neroli Bigarade pétalo") had the following constants:—d_{15° 0.8798 and 0.8686; α_{D15° + 12° 4′ and 12° 12′; n_{D15° 1.4739 and 1.4760; soluble in 1 vol. and in 1.4 vol. 90 per cent. alcohol,

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[1]) As regards sweet Spanish orange oils see also p. 21 of this *Report*. —

[2]) So far as we are aware citral had not yet been identified in sweet orange peel oils. —

[3]) We are not aware that citral had previously been found in mandarin oil.

with more and with 4 vol. turbidity; acid v. 0.3 and 2.22; ester v. 42.31 and 31.82 (corresponding to 14.81 per cent. and 11.13 per cent. of linalyl acetate); ester v. after acetyl. 131.12 and 117.0 (corresponding to a total alcohol percentage of 37.75 and 33.78 and a free alcohol percentage of 25.84 and 25.02). The alcoholic solutions of the oils were fluorescent.

A *Sweet Orange Blossom Oil* from Sevilla ("Portugal extra") gave the following properties: — d_{15° 0.8554; α_{D15° + 41°36′; n_{D15° 1.7444; soluble in 8 vol. 90 per cent. alcohol; acid v. 3.43; ester v. 15.10, 5.29 per cent. of linalylacetate; ester v. after acetyl. 76.48; total alcohol 23.33 per cent., free alcohol 16.48 per cent.

The following *Rue Oils* came partly from *Ruta montana*, L. (the oil from Malaga, certainly, the oils from Cordoba and Sevilla most likely), partly from *Ruta bracteosa*, L., or *Ruta graveolens*, L. (the oil from Carcagente).

Spanish Rue Oils.	Carcagente.	Cordoba.	Sevilla.	Malaga.
d_{15°	0.8839	0.8329	0.8350	0.8364
α_{D8°	+ 0°24′	+ 0°2′	+ 0°52′	+ 0°44′
n_{15°	1.4320	1.4328	1.4333	1.4318
Solidification point	starting at + 3°, still incomplete at − 10°.	starting at + 13°	+ 8° to + 10°	+ 10° to + 11°
Solubility in alcohol of 70 per cent.	1:2.5	1:2.5	1:25 ?	1:2.5
Acid v.	4.4	1.8	2.25	1.3
Ester v.	3.87	4.65	5.60	8.50
ketones (hydroxylamine method) calculated as				
methylheptylketone	—	—	81.1 per cent.	72 per cent.
methylnonylketone	—	—	97.1 per cent.	86.4 per cent.
Ester v. after acetyl.	24.04	10.86	18.02	—

The oil from Cordoba gave in the Ladenburg flask at 710 mm. the following fractions: — 195 to 210°, 7.58 per cent.; 210 to 215°, 16.60 per cent.; 215 to 220°, 21.72 per cent.; 220 to 225°, 21.55 per cent.; 225 to 230°, 23.13 per cent.; 230 to 240°, 7.24 per cent.; residue 2.18 per cent. The three first fractions (methylheptyl ketone and methylnonyl ketone) did not solidify at 0°; the second and third fractions displayed a strong bluish fluorescence (methylester of the methylanthranilic acid). The fourth and fifth fractions solidified at + 10° and + 11° and did not fluoresce. From the last fractions caprinic acid (m. p. 28 to 31°) was obtained by oxidation with sodium hypobromite.

Another rue oil from Cordoba, yielding 6 fractions between 210 and 242°, showed no fluorescence and did not contain any methylheptyl ketone, but did contain methylnonyl ketone. Consequently the Spanish rue oils might be traced back to 2 types, the one of oils with a high solidification point, between 10 and 12°, not fluorescent, and the other fluorescent and of a lower solidification point.

Of all the *Geranium Oils* the Spanish is the most highly esteemed on account of its delicate odour. Of three authentic oils from Sevilla, Malaga and Valencia the first seemed to be adulterated, being insoluble in 3 vol. 70 per cent. alcohol. The other two oils had the following constants: — d_{15° 0.8828 and 0.9012; α_{D15° − 11°24′ and − 9°10′; n_{D15° 1.4715 and 1.4730; soluble in 1.5 vol.¹) and in 1 vol. and more 80 per cent. alcohol, soluble in 2.5 vol.¹) and in 2 vol. and more 70 per cent. alcohol; acid v. 10.40 and 7.00;

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¹) On addition of 4 to 5 vol. of alcohol the mixture turned turbid and paraffin crystals appeared.

ester v. 59.63 and 56; tiglinate 25.14 per cent. and 23.60 per cent.; ester v. after acetyl. 208.65 and 220.27. Total alcohol ($C_{10}H_{18}O$) 67.96 per cent. and 77.1 per cent.; free alcohol 46.14 per cent. and 51.5 per cent.

Two *Bitter Almond Oils* from Sevilla (containing prussic acid) and one from Valencia (free of prussic acid) had the following properties:— Both were faintly-yellow, had the characteristic smell and were optically-inactive:—d_{23° 1.045 and d_{15° 1.0674; n_{D23° 1.5419 and 1.5440; prussic acid 0.843 per cent. (by weight) or 0.862 per cent. (by volume); soluble in any proportion in 90 per cent. alcohol and soluble in 0.5 vol. 80 per cent. alcohol (both), and in 1.5 vol. and 1.4 vol. 70 per cent. alcohol.

Four *Fennel Oils*[1]) from Sevilla (of 1915), Cordoba (1912 and 1914) and Del Padul, Granada (1916) had the following constants:—$d^{20^\circ}_{15^\circ}$ 0.8923 to 0.9212; $\alpha_{D20^\circ} + 46^\circ 36'$ to $+ 55^\circ 8'$; n_{D20° 1.4842 to 1.5020; soluble in 0.3 to 1.0 vol. 90 per cent. alcohol, in 15 to 20 vol. 80 per cent. alcohol; solidification point below -10° and below -13°; acid v. 0 to 3.2; ester v. 3.2 to 16.9; fenchyl acetate[2]) 1.99 to 5.92 per cent.; ester v. after acetyl. 17.3 to 46.0; total alcohol 4.76 to 12.65 per cent.; free fenchyl alcohol 3.88 to 8.18 per cent.; anethole and estragol (methyl chavicol) 24.76 to 39.36 per cent.; fenchone 15.04 to 20.69 per cent. These figures indicate that these products (at any rate the partly-bitter fennel oils) do not correspond to the fennel oils of other countries. Dorronsoro ascribes this fact to the circumstance that the manufacturers submit, not the fruit, but the whole plant to distillation in order to secure a higher yield.

The two oils from Cordoba yielded in a Ladenburg flask 7 fractions between 155 and 230° (705 mm.), of which the first ones had a very high specific rotation ($\alpha_{D15^\circ} + 74^\circ 30'$ and $+ 81^\circ 44'$). From the fifth and sixth fractions (between 200 and 228°) the anethole separated at low temperatures and could thus be obtained. In the sixth and seventh fractions, which were distinguished by a high specific gravity and high refractive index, ethylfenchyl alcohol (inactive) was present. The substance is not further identified in the memoir.

A *Master Wort Oil* from Carcagente (Valencia)—the mother plants, *Peucedanum Ostruthium*, Koch (*Imperatoria romana;* known under this name in Spain) and *Peucedanum Hispanicum*, B., are frequent in the east and south of Spain—was a yellow, transparent liquid of an agreeable sweetish odour reminding of pine leaf oil:—d_{15° 0.8611; $\alpha_D + 44^\circ 56'$; n_{D15° 1.4800; soluble in 5 vol. 90 per cent. and in 22 vol. 80 per cent. alcohol; acid v. 2.6; ester v. 19.6 (corresponding to 6.93 per cent. of ester $[C_{10}H_{19}O \cdot CO\,CH_3]$); ester v. after acetyl. 44.21 (corresponding to 6.99 per cent. of free alcohol and to 12.74 per cent. of total alcohol).

From Carcagente and Malaga originated two *Eucalyptus Oils* of the following constants:—d_{15° 0.9300 and 0.9117; $\alpha_D + 1^\circ 38'$ and $4^\circ 14'$; n_D 1.4672 and 1.4662; soluble in 90 per cent. alcohol and in 0.4 vol. 90 per cent. alcohol (turbidity with 2 vol.), in 1 vol. and in 1.5 vol. (turbidity) 80 per cent. alcohol, in 2.5 vol. and in 15 vol. (turbidity) 70 per cent. alcohol; acid v. 2.37 and 1.77; ester v. 15.82 and 13.66; cineole percentage 53 and 65.5 (resorcinol method). The distillation in a Ladenburg flask yielded the following fractions:—162 to 167°, 8.17 per cent.; 167 to 170°, 15.90 per cent.; 170 to 173°, 30.04 per cent.; 173 to 180°, 11.92 per cent.; 180 to 183°, 14.00 per cent.; residue 19.97 per cent. The high residue percentage is striking.

The following two oils of *Peppermint* came from Sevilla and Valencia; it is not certain, however, whether they had been prepared from Spanish or from foreign

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[1]) The constants suggest the presence, at least partly, of bitter fennel oils. — [2]) It is not stated how the fenchyl alcohol was identified; *d,l*-fenchylalcohol had so far been found only in American wood turpentine oil; cf. *Report* April **1910**, 108.

peppermint. The oils were colourless and yellowish-green and had the following properties which testify to their good quality:—d_{15° 0.9080 and 0.9071; α_{D15° — 23°32′ and —25°8′; n_{D15° 1.4596 and 1.4615; soluble in 90 per cent. alcohol, in 1 vol. and in 3 vol. 80 per cent. alcohol, in 2.5 vol. and in 3.5 vol. 70 per cent. alcohol; acid v. 0 and 1.2; ester v. 16.71 and 29.29; menthylacetate 5.85 per cent. and 10.35 per cent.; ester v. after acetyl. 165.68 and 188.5. Total menthol 52.66 and 61.16 per cent.; free menthol 46.67 and 50.35 per cent.

Very different from one another in their properties were two oils, the one from *Mentha viridis*, L., from Carcagente, and the other from *Mentha sativa*, L., from Malaga. Both kinds are popularly known as *Yerbauena*. The first product had an intense yellow colour and smelled of wild mint *(Mastranzo)*; the second oil was yellowish-green, smelled strongly of peppermint and had a sharp, bitter taste reminding of mint. The constants were:—d_{15° 0.950 and 0.9385; α_{D15° — 3°15′ and +19°50′; n_{D15° 1.4914 and 1.4865; soluble in 0.5 vol. (with more alcohol turbidity) 90 per cent. alcohol and in all proportions in 90 per cent. alcohol, in 1 vol. 80 per cent. alcohol and in all proportions in 80 per cent. alcohol; insoluble in 20 vol. and soluble in 4 vol. 70 per cent. alcohol; acid v. 2.4 and 1.98; ester v. 53.1 and 10.56; menthylacetate 18.78 per cent. and 3.72 per cent.; ester v. after acetyl. 141.2 and 37.16. Total menthol 41.7 and 10.64 per cent.; free menthol 24.57 and 9.26 per cent. Menthone 0.77 per cent. and 0 per cent.

Six different *Pennyroyal Oils* from *Mentha Pulegium*, L., coming from Cordoba, Sevilla, Jaën, Malaga, Alhaurin de la Torre and Alhaurin el Grande, were distinguished by their high quality; most of them contained 80 to 90 per cent. of pulegone. The constants were:—d_{17° 0.934 to 0.948; α_{D18° +16°12′ to +22°12′; n_{D18° 1.4840 to 1.4864; entirely soluble in 90 per cent. alcohol, soluble in 0.8 to 1.2 vol. 80 per cent. alcohol, soluble in 1.2 to 1.8 vol. 70 per cent. alcohol; acid v. 2.02 to 14.8; ester v. 7.4 to 13.2; menthyl acetate 2.61 to 4.67 per cent.; ester v. after acetyl. 32.25 to 42.0; total alcohol 9.23 to 12.08 per cent., free alcohol 7.06 to 8.95 per cent.; pulegone content (sulphite method) 82 to 90 per cent. The distillation of the Cordoba oil in a Ladenburg flask (710 mm.) yielded the following fractions:—205 to 209°, 5.75 per cent.; 209 to 216°, 24.63 per cent.; 216 to 217°, 21.91 per cent.; 217 to 219°, 22.96 per cent.; 219 to 222°, 11.45 per cent.; 222 to 223°, 3 per cent.; residue 10.30 per cent. Above 223° decomposition of the oil set in.

Five *Sage Oils*, which had been obtained in the years 1911 to 1915 from *Salvia lavandulaefolia*, Vahl. (determined by D. Blas Lazaro) which is common particularly in Andalusia, showed very different behaviours:— d_{15° 0.908 to 0.9327; α_{D15° —12°44′ to +20°50′; n_{D20° 1.4672 to 1.4739; acid v. 0.45 to 1.14; ester v. 5.7 to 35.7; ester v. after acetyl. 29.6 to 76.0; ester (calculated as linalyl acetate) 2.0 to 12.5 per cent.; total alcohol 8.34 to 20.9 per cent.; free alcohol 5.89 to 11.45 per cent.; soluble in 0.3 to 0.5 vol. 90 per cent., partly in any proportion; soluble in 1.8 per cent. to 20 vol. 80 per cent. alcohol; soluble in 3.3 to 30 vol. 70 per cent. alcohol.

The sage oil from Albuñuelas (province of Granada) has more fully been investigated by Dorronsoro. He distilled at 710 mm. pressure the following fractions: — 164 to 170°, 9.5 per cent.; 170 to 180°, 38 per cent.; 180 to 190°, 15.3 per cent.; 190 to 203°, 8 per cent.; 203 to 215°, 25 per cent.; residue 4 per cent. The last fraction solidified partly. Another, larger portion of the oil was distilled at reduced pressure, repeatedly in several fractions. In this the following constituents were identified:— cineole was present in large quantities (resorcinol compound); *d*-camphor (m. p. 178°; oxime m. p. 128); linalool (conversion into citral by means of chromic acid mixture); linalyl acetate and *iso*-valerate. Camphene was probably present; from the fraction 170 to 180°, a white body, m. p. 135 to 136° (camphene-camphoric acid) was obtained by treatment with potassium permanganate. The identification of pinene and dipentene was uncertain. The fraction 156 to 160° yielded directly a nitrosochloride of m. p. 103° (pinene nitrosochloride melts at 103°). Dissolved in chloroform and reprecipitated by methyl alcohol, the body had, however, assumed a melting point of 93 to 94° and gave a nitrolbenzylamine of m. p. 103 to 104° instead of 122°. This circumstance points to the simultaneous presence of a second terpene, possibly dipentene, the nitrolbenzylamine of which melts at 110°.

In the distillation of the Spanish *Rosemary Oil*, use was frequently made also of other labiates, like spike lavender and sage. The circumstance may account for the varying quality of this oil which in the pure state is said to be better than the French and Dalmatian product. Dorronsoro investigated the authenticated rosemary oils obtained from fresh herbs in blossom from the provinces of Granada, Jaën, Malaga and Murcia. The oils, which had been prepared in the years 1911, 1914, 1915 and 1916, had been preserved in well-closed vessels protected from the light. Of the samples, six were feebly dextro-rotatory and two feebly laevo-rotatory:— d_{15° 0.8864 to 0.9083; α_{D15° — 4°0′ to + 6° 56′; α_D of the first tenth of the distillate — 5° 28′ to + 5° 30′; n_{D15° 1.4672 to 1.5402; soluble in 0.3 vol. to 0.8 vol. 90 per cent. alcohol, in 0.5 to 15 vol. 80 per cent. alcohol (6 oils were insoluble in 70 per cent. alcohol); acid v. 0.57 to 2.08; ester v. 4.6 to 11.8; ester v. after acetylation 28.27 to 81.21; bornylacetate 1.61 to 3.88 per cent.; total alcohol 7.94 to 28.42 per cent.; free alcohol 5.39 to 25.02 per cent.

The distillation (708 mm.) of an oil from Albuñuelas yielded the following fractions:— 152 to 163°, 24.3 per cent.; 163 to 166°, 17.10 per cent.; 166 to 170°, 14.6 per cent.; 170 to 180°, 16.6 per cent.; 180 to 190°, 9.4 per cent; 190 to 200°, 4.6 per cent.; 200 to 210°, 5.9 per cent.; residue 7.5 per cent. The first two fractions gave a good yield of pinene nitrosochloride, m. p. 103°. The fractions 4 and 5 gave the cineole reaction distinctly. From the seventh fraction camphor could be obtained, which soon turned solid. Other products present were acetic acid and *iso*valeric acid, probably also thymol and linalool.

The source of the Spanish *Oil of Lavender*, as gained particularly in Andalusia, must according to Blas Lazaro be found in *Lavandula latifolia*, Will. (*L. spica*, L. var. *latifolia*). Eight lavender oils from Albuñuelas, Valencia, Granada, Jaën and Murcia had the following constants:—d_{15° 0.903 to 0.9161; α_{D15° — 3° 28′ to + 10° 54′; n_{D15° 1.4650 to 1.4718; acid v. 1.06 to 3.2; ester v. 5.32 to 14.2; ester v. after acetyl. 90.3 to 106.2; linalyl acetate 1.86 to 4.97 per cent.; total alcohol 26.5 to 31.72 per cent.; free alcohol 28.85 to 27.95 per cent.; soluble in 1.7 to 2.2 vol. 70 per cent., soluble in 2.7 to 4.3 vol. 65 per cent. alcohol.

From the mountains of Granada, Albuñuelas, came an authenticated oil of *Lavandula Stœchas*, L. (*cantueso*). The product was transparent, reddish-yellow, had a pleasant smell of camphor and the following constants:—d_{16° 0.9485; α_D + 36° 10′; n_{D15° 1.4768; soluble in 2.6 vol. 70 per cent., in 1.5 vol. 80 per cent. and in any proportion in 90 per cent. alcohol; ester v. 20.95 (corresponding to 7.33 per cent. of bornyl acetate); ester v. after acetyl. 32.4 (corresponding to 3.18 per cent. of free borneol and 9.13 per cent. of total borneol). In the Ladenburg flask at 710 mm. the following fractions were obtained:— 180 to 183°, 6 per cent.; 183 to 190°, 37 per cent.; 190 to 200°, 35 per cent.; 200 to 210°, 13 per cent.; 210 to 215°, 4.5 per cent.; residue 4.5 per cent. Most of the last fraction solidified; to judge by the form and smell of the crystals the substance was camphor. Dorronsoro further distilled 500 g. of oil at 16 mm. He could not find any terpene in the 5 g. of distillate passing below 100°, nor were there any terpenes

Distillation of Linaloe Oil in Chiautla, Mexico.

(After a water-colour painting in the possession of the Perfumery Department of the German Museum in Munich. Gift of the firm of Schimmel & Co.)

nor thujone present in the other fractions above 100°. On the other hand a semicarbazone melting at 210° was found which Dorronsoro regards as a mixture of fenchone and camphor semicarbazones. The oxime of *d*-fenchone (white needles, m. p. 156 to 160°) was obtained. The oil contained altogether 46.80 per cent. of ketones (*d*-fenchone + camphor, reduction method). A large quantity of cineole was determined by means of the hydrobromic and the phosphoric acid methods. The iodole reaction was doubtful.

Another sample of oil from *Lavandula Stœchas* from Malaga gave the following constants:—d_{15° 0.9470; $\alpha_D + 45^\circ 44'$; n_D 1.4682; entirely soluble in 90 per cent. alcohol, soluble in 1 vol. 80 per cent. and in 1.5 vol. 70 per cent. alcohol; acid v. 2.25; ester v. 13.43 (corresponding to 4.72 per cent. of bornyl acetate)[1]).

The *Thyme Oils* manufactured in Spain come from different species which Blas Lazaro identifies as *Thymus vulgaris*, L., *Thymus Zygis*, L., *Thymus hyemalis*, Lg. and *Corydothymus capitatus*, Rchb. Since the products obtained from the thyme species contained much less phenol bodies than the oil from the corydothymus, we should have to distinguish two main classes of Spanish thyme oils. The oils poor in phenols are not so much sought after as those rich in phenols. For that reason the manufacturers, especially in Andalusia, mix the two sorts in order to prepare an average quality of 40 per cent. of phenols. The thyme oil is, however, often blended also with sage oils.

Dorronsoro studied three oils of thyme species from Albuñuelas and Jaën and eight oils of the corydothymus from Granada, Cadiz, Malaga and Cordoba and found for the former the density constants d_{15° 0.908 to 0.917 and phenol contents of 34 to 38 per cent. The latter had the specific gravity d_{15° 0.9343 to 0.9847 and phenol contents of 64 to 67.5 per cent.

In this connection we may draw attention to a publication by E. J. Parry[2]). Parry accentuates that six Spanish typical thyme oils which he investigated contained thymol, but no carvacrol. So far carvacrol had frequently been found to be the main constituent of Spanish thyme oils. Parry believes that the continuously-increasing demand for Spanish oils has induced the manufactures to lay more stress upon the supply of an unobjectionable uniform raw material. Formerly the Spanish products had mostly been distillates of more than one kind of plant.

In investigating the oil of *Thymus Mastichina*, L., in Spain called *Mejorena silvestre*, Dorronsoro observed that another species of thyme which thrives in Almeria, *Thymus cephalotus*, L., gave an essential oil of quite similar properties. Four oils of *Thymus Mastichina* from Albuñuelas, Malaga and Granada had the following constants:—d_{15° 0.915 to 0.9168; $\alpha_{D15^\circ} + 2^\circ 22'$ to $+ 4^\circ 14'$; n_{D15° 1.4640 to 1.4693; acid v. 0.3 to 1.4; ester v. 8.32 to 19.7; ester v. after acetyl. 49.30 to 54.5; ester (linalyl acetate) 2.91 to 6.90 per cent.; total alcohol 14.07 to 11.18 per cent.; soluble in 90 per cent. alcohol, soluble in 1 to 1.3 vol. 80 per cent. alcohol, soluble in 2 to 3.5 vol. (with 12 vol. turbidity) 70 per cent. alcohol; cineole contents (resorcinol method) 60 to 62 per cent. In an oil from *Thymus cephalotus* from Almeria the following constants were found:—d_{15° 0.916; $\alpha_{D15^\circ} + 4^\circ 14'$; n_{D15° 1.4690; acid v. 0.5; ester v. 7.74; ester v. after acetyl. 50.4; ester (linalyl acetate) 2.72 per cent.; total alcohol 12.12 per cent.; soluble in 2.5 vol. 70 per cent. alcohol; cineole (resorcinol method) 60 per cent.

Under the name of *"Tomillo limonero"* a labiate, smelling of lemon oil, is known in Spain which Lazaro identified as *Thymus hirtus*, Willd. We investigated the essential

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[1]) The rotation to the right suggests that Dorronsoro dealt with oils of *Lavandula dentata;* for the oil of *L. Stœchas* is, according to our observations, lævorotatory. — [2]) *Perfum. Record* **11** (1920), 139.

oil of this plant already years ago¹); but we were then only able to ascertain as regards its botany that, according to Parry and Bennett a similar product, known as thyme lemon oil, was supposed to come from *Lippia citriodora,* Kth. We questioned this statement already at that time, and the researches of Dorronsoro have now proved that the oil in question did not come from a verbena, but from *Thymus hirtus.* The sample of this oil from the year 1915 which Dorronsoro studied, was brown, transparent, smelled of oil of lemon and had the following constants:—d_{15° 0.909; α_{D15° $+13^\circ 20'$; n_{D15° 1.4825; soluble in 90 per cent. alcohol, soluble in 2 vol. 80 per cent. alcohol and in 7 vol. 70 per cent. alcohol; acid v. 4.2; ester v. 18.34; ester v. after acetyl. 95.35; ester (acetate of an alcohol $C_{10}H_{18}O$) 6.42 per cent.; total alcohol ($C_{10}H_{18}O$) 28.35 per cent.; free alcohol 22.52 per cent.; citral contents (bisulphite method) 6.6 per cent., (hydroxylamine method) 12.54 per cent. (by weight). In the Ladenburg flask:—155 to 173°, 9.05 per cent.; 173 to 180°, 9.80 per cent.; 180 to 190°, 18 per cent.; 190 to 200°, 19.11 per cent.; 200 to 210°, 23.25 per cent.; 210 to 220°, 8.92 per cent.; 220 to 225°, 6.5 per cent.; residue 5.82 per cent. The first two fractions probably contained *d*-limonene (20 to 25 per cent., b. p. 175 to 176°, d_{15° 0.850), the fraction 190 to 220° probably linalool and chiefly *d*-fenchone (semicarbazone m. p. 176 to 178°). Dorronsoro considers on the strength of his investigations, though they are not completed yet, that the oil has the following compositions:—terpenes (limonene) 20 to 25 per cent.; citral 12.54 per cent.; ester (acetate of an alcohol $C_{10}H_{18}O$) 6.50 per cent.; free alcohol $C_{10}H_{18}O$ 22.60 per cent.; fenchone, resins &c. 33.36 per cent.

Two yellowish, almost colourless oils of the cultivated *Marjoram* (*Origanum Majorana,* L.), from Malaga and Sevilla had the following constants:—d_{15° 0,8956 to 0.8601; α_{D20° $+17^\circ 12'$ and $+10^\circ 26'$; n_{D20° 1,4744 and 1.4787; acid v. 1.84 and 1.3; ester v. 30.70 and 8.63; ester v. after acetyl. 62.67 and 68.94; ester (terpinyl acetate) 10.75 and 3.02 per cent.; total terpineol 18.07 and 19.9 per cent.; free terpineol 9.0 and 17.37; soluble in any proportion in 90 per cent. alcohol, in 1.7 vol. (with 5 vol. more, turbidity) and in 1.5 vol. (with 3 vol. more, turbidity) 80 per cent. alcohol; ketone contents (hydroxylamine method) 9.26 and 6.9 per cent., (bisulphite method) 8 per cent.

A *Melissa Oil* (*Melissa officinalis,* L.) from Sevilla had the following properties:—d_{25° 0.8910; α_{D22° $+2^\circ 8'$; n_{D22° 1.4704; soluble in 0.5 vol. 90 per cent. and in 2 vol. 80 per cent. alcohol (slight turbidity with more); acid v. 2.2; ester v. 27.42; ester v. after acetyl. 236.28; aldehydes (bisulphite method) 42 per cent.

Three *Verbena Oils* from Sevilla, Malaga and Valencia, from *Lippia citriodora,* H. B. et K. (*Verbena triphylla,* L., *Aloysia citriodora,* Ort. *[Yerba Luisa]*), were of a golden-yellow colour and smelled more or less strongly of lemon oil. The Malaga oil which was distinguished by its high rotation, α_{D22° $+15^\circ 52'$, had a penetrating smell reminding of camphor. The constants were:—d_{15° 0.9059, 0.9060, 0.8820; α_{D22° $+1^\circ 28'$, $+15^\circ 52'$, $\pm 0^\circ$; n_{D22° 1.4778, 1.4802, 1.4835; soluble in any proportion in 95 per cent. alcohol and in 90 per cent. alcohol; in 0.3 vol., in 1 vol. (with more, turbidity) 90 per cent. alcohol, in 1 vol., in 1.8 vol. (with more, turbidity); insoluble in 14 vol. 80 per cent. alcohol. Aldehyde contents (sulphite method) 40 p. c., 30 p. c., 68 p. c.; (hydroxylamine method) —, 37.7 p. c., 66.5 p. c.; acid v. 6.17, 2.71, 1.5; ester v. 43.17, 16.31, 10,49; ester (geranyl-acetate) 15.09 p. c., 5.71 p. c., 3.67 p. c.; ester v. after acetyl. 185.77, 156.80, 205.8; total alcohol 51.95 p. c., 48.80 p. c., 66.84 p. c.; free alcohol 39.42 p. c., 43.15 p. c., 62.90 p. c.

An oil obtained from cultivated *Wormwood* from Malaga was intense greenish-blue, opaque, had the sharp smell of the plant and tasted bitter and of camphor (thujone?):—

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¹) *Report* April 1907, 101.

d_{15° 0.9156; soluble in one vol. 90 p. c., in 4.5 vol. 80 p. c., and in 15 vol. 70 p. c. alcohol; ester v. 27.64, thujyl acetate 9.67; ester v. after acetyl. 38.35; total thujyl alcohol 10.47 p. c.; free thujyl alcohol 3.10 p. c.; thujone (by hydrogenation) 57.50 p. c.

Dorronsoro no doubt deserves all thanks for having made us acquainted with so large a number of Spanish oils, and his research may probably induce many another worker to compile a similar publication on these oils which have on the whole very little been studied so far. It would be recommendable in future cases, however, to experiment with the fresh distillates of botanically-well identified materials, which can not always be said of Dorronsoro.

It is well known that *Cyprus* exports various kinds of agricultural produce like wheat and barley, St. John's bread, wine, raisins, fruit, and cotton. Although the essential oils, which are of significance in the industry, cannot in importance be compared with these chief products, yet a summary of the plants, of special interest for us, which this fertile island produces, will be appropriate. We take the following data concering the agriculture and the produce of Cyprus from W. Bevan[1].

Agrumen, like *Citrus* species, *Orange* and *Bergamot trees*, are distributed all over the island. The sweet orange tree, to be found everywhere, particularly however in Famagusta, gives the best fruit, the thick-fleshy, oval Jaffa orange. Bitter oranges are everywhere grown from seeds as wild plants, subsequently to be grafted. The Government arboreta supply many thousands of wild and grafted orange trees per annum. From time to time much produce has been lost by diseases, and in 1899 whole groves of oranges had to be derooted or cut down quite short in Famagusta, Lefka, and Kythrea, Gradually people learnt how to fight these plagues and how to raise the production, although the gum disease (gummosis)[2] and the scale disease are still doing injury. The native planters still commit the mistake of placing the trees too close to one another and keeping them too moist. They are short-sighted and believe that, the more plants per acre, the greater the profit. Water is a precious article in Cyprus; consequently they fancy to stimulate every plant by ample supply of water. In reality this watering impairs the orange and lays the foundation to the gum disease. There are no statistics extant as to the manufacture of the essential oils of the agrumen fruits on the island of Cyprus and as to their utilisation. Up till 12 years ago much of this fruit was exported to Rumania and Russia. As, however, the oranges from Cyprus frequently suffered from the scale disease and sometimes rotted already during the transport, this export declined. At present the fruit is still being shipped only to Egypt.

Of other plants which are sources of essential oils we find in Cyprus coriander, *Coriandrum sativum*[3], L., anise, *Pimpinella anisum*[4], L., Roman caraway, *Cuminum Cyminum*[5], L., the fennel flower, *Nigella sativa*, L., the laurel tree, *Laurus nobilis*[6], L., the rose shrub, *Rosa damascena*, Mill., the oassie shrub, *Acacia Farnesiana*, Willd., and various species of *Origanum*[7].

Rose oil had been distilled since 1897 in a small quantity and a primitive manner in the village of Milikouri where the damascene rose is growing plentifully. When during the war the Bulgarian rose industry diminished, Cyprus began to expand its cultivation once more. The Agricultural Department appointed technical experts who

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[1] *Bull. Imp. Inst.* **17** (1919), 344, 503. — [2] Amber-yellow secretions appear on the bark which harden on exposure to the air and resemble gum Arabic in their properties. The bark splits and finally peels in spots. (A. Risso et A. Poiteau, *Histoire et culture des orangers.* Paris **1872**, p. 200.) — [3] Cf. *Report* **1918**, 18. — [4] *Ibidem* **1918**, 68. — [5] *Ibidem* **1918**, 21. — [6] *Ibidem* April **1914**, 66. — [7] Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III. p. 480 and 486.

control the rose oil manufacture in Milikouri and introduce better methods of distillation. In its constants the Cyprus oil distilled in 1917 agreed almost completely with those of Bulgarian oil of rose. The smell of the Cyprian product was quite good, though rather feeble. The price offered for the oil (70 s. per oz.) was not bad, when one considers that French oil was sold at the rate of 78 to 85 s. per oz.

The *Cassie Shrub, Acacia Farnesiana,* Willd., the flowers of which are utilised in France for the preparation of scent, occurs only sparely on the island of Cyprus, but in strong and healthy specimens. As cognate species are frequently found on the island, we may assume that the variety which is valuable for its scented flowers might be further distributed. The cassie shrub, which is known in various countries under all sorts of names (dune rose, sweet briar in Barbados, stinking cassie in Antigua, cassier in the south of France), is called *Skouroupathos* or *Skouroupathia* by the inhabitants of Cyprus. The same name is given to a weed, related to cassie and to be found almost on any field, which is very hard to extirpate owing to its deeply-penetrating roots.

Origanum Oil from Cyprus, the mother plant of which has not yet been identified with certainty, has since 1899 been prepared under Government control. The last English communication confirmed former investigations (Imperial Institute, London, and Schimmel & Co.[1]) which did not agree with the statement made by the Government analyst, that the origanum oil from Cyprus was rich in carvacrol (80 per cent.). Frequent analyses, moreover, revealed that the composition of the product was not always the same. As the oil darkens rapidly when exposed to light and air, the Imperial Institute has worked out a method by means of which the rectified oil can be kept colourless for a long period.

In 1910 people were permitted to gather the wild plant in the forests; private people then began, in addition to the Government, to distil origanum oil. At present about 2750 lbs. of oil are prepared every year. Prices have steadily been going up, from 3/– per lb. to 8/6 d. per lb. Whilst before the war the transport to London cost £ 8 per ton, £ 200 are now demanded per ton, and it is no wonder that the oil of 1917 is still in the docks of Alexandria.

Only within the last years a commencement has been made on the *Philippines* to manufacture, on a larger scale, essential oils from the plants which are natives of these islands and which supply *Odorous substances,* such as ylang-ylang, champaca, lemongrass, vetivergrass, *Cinnamonum Mercadoi,* Vid. and ginger. According to A. N. Luz[2]) the erection of works with modern equipment is contemplated on the island. The article by Luz, which contains much that was already known[3]), may be extracted to supplement previous communications.

The *Ylang-Ylang tree, Cananga odorata,* Hook. f. et Thomson *(Anonaceæ),* is particularly characteristic for the Philippine Islands. The ylang-ylang oil there obtained is distinguished by its fine quality from the oils of other tropical countries. 350 kg. of blossoms are required for the preparation of 1 kg. of first-class oil, which is sold at 100 dollars; less superior kinds of oil can be bought for 15 to 35 dollars. The blossoms, the treatment of which requires experience and care, are generally plucked over night and then gathered in the morning in such a manner that they are only piled up in small heaps and then taken to the still houses.

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[1]) Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. III, p. 487; *Report* **1918**, 37. — [2]) *Americ. Perfumer* **15** (1920), 216. — [3]) Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. II, p. 393, 375, 209, 445.

The *Champaca tree, Michelia Champaca,* L. *(Magnoliaceæ)* is likewise cultivated on the Philippines for its scented flowers. From its fifth year the plant blossoms once every year for 3 months, and the lowest yield of the blossoms of one tree amounts to about 4.50 dollars. According as one plants the champaca tree on the square system (::) or on the quincunx system (:·:), there will be 176 or 220 plants per hectare[1]. With the square arrangement other useful plants like lemongrass may be raised as intermediate culture between the champaca trees, and this former system is therefore considered the more profitable. When we assume that on average there will be about 200 plants per hectare, a champaca plantation of 1 hectare would bring in at least 900 dollars and, after deduction of all expenses, 683 dollars per year.

The so-called *West Indian Lemongrass, Andropogon citratus,* D.C., which occurs in many tropical countries, mostly in the cultivated condition, is not much cultivated on the Philippines, but grows wild on the whole island and abundantly especially in the high lands of Benguet. So far the plant has specially been utilised in the kitchen, as an addition to baths, for incense, and also as an external remedy against headache. The lemongrass plant growing quickly and thriving without any care, its cultivation especially as intermediate product is recommended, since the demand for lemongrass oil is increasing. The grass may be cut three or four times a year; 496 lb. of fresh herb give 1 lb. of crude oil. The annual yield per acre would therefore come to 20 lb. of crude oil. From well-dried leaves, which have lost 70 per cent. of their weight, 0.8 to 0.85 per cent. of oil[2] may be obtained, whilst the fresh-collected leaves yield 0.2 per cent. in the rainy season and 0.55 per cent. of oil in the dry season. Nursery experiments show that young leaves contain a higher percentage of oil than old leaves, and that 3 mowings a year give better results than 2 mowings.

The *Vetiver grass, Vetiveria zizanioides,* Stapf, is also common all over the Philippines. The roots, which the natives call *Moras* or *Raiz de Moras,* are commonly put into the clothes to make them pleasant-scented. Their contents in essential oil varies with the origin of the roots. Bacon obtained from fresh, crushed roots 1.09 per cent. of oil. Crops of up to 60 kg. of roots are said to have been obtained from 100 plants. In reality 100 plants grown in sandy soil in Paranaque, three to four months old, gave only 23 kg. of roots which, however, had a high oil percentage. The drug can be bought on all the public markets at 7½ or 12½ cents per kg., 1 kg. of oil of good quality is valued at 50 to 100 dollars. So far this oil has only been prepared in Europe, and chiefly from roots of Indian origin.

Cinnamomum Mercadoi, Vid., a big tree called *Calingag* by the Tagals, occurs chiefly in the provinces of Davao, Rizal, Pampanga, Bataan, Camarines and Tayabas. Frequently up to 150 trees are found per hectare, the bulk of which yields an oil resembling sassafras in its smell. 25 kg. of the bark of a tree on Bataan gave 260 g. of a light-yellow oil. According to older statements of travellers the *Cinnamomum zeylanicum,* Nees is also said to occur on the island of Mindanao.

Ginger is everywhere to be found on the Philippines, but has so far not been exported. It is cultivated on a small scale and serves as a condiment for food. 132 kg. of cut native roots yielded on distillation 95 g. of a pale yellow oil which smelled of ginger and also strongly of orange-peel oil. Another experiment with 50 kg. of the drug yielded 25 g. of oil. The yield of a ginger field frequently comes up to 1100 to 2200 kg. of roots per hectare. Although the drug fetches a good price, the high expenses do not

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[1] 1 hectare = about 2½ acres. — [2] The English report speaks of 8.2 and 5.5 per cent. of oil. The figures are apparently misprints, as the previously-made statements concerning the oil yield were quite correct.

leave much margin for of a clear profit. The cultivation requires much expensive manual labour, and the ginger plants exhaust the soil, so that repeated cultivation of the same ground is only possible with the aid of good manuring.

According to G. B. Roncagliolo[1]) the chances of a *Italian floral perfumery industry* are very favourable, though the industry has not yet received there the same attention as in other countries. For the purpose of promoting the perfumery industry the Italian Government, he states, issued in 1918 and 1919 decrees which exempt the horticulturists and distillers of essences for a long time from any taxes. As a matter of fact a number of companies have been founded within a short period of time for the production of odoriferous substances and for the preparation and the trade in perfumes. The nurserymen have likewise enlarged their concerns, and especially in the coastal districts of Western Liguria, in Ventimiglia, Bordighera, Ospedaletto, San Remo and Taggia, the cultivation of roses and of violets has much increased. Although the roses were exported to France in weights of nearly half a million kg., the plant is also worked up in Italy itself (Milan) in considerable quantities and converted into a relatively inexpensive perfume. The peppermint which is cultivated in Pancalieri, San Antonio di Succi, Azeglio (Ivrea), Fenestrella (Pinerolo) and Affori (Milan)[2]) yielded an oil which was considered unsurpassed[3]) in finesse and quality. In the year 1913 peppermint oil to the value of one million lire was said to have been exported, and more than 30 000 kg. of this oil to have been distilled near Pancalieri in 1914. The export of orris roots[4]), of which some 200 000 kg. were gained in Italy per year, was also called important.

Under the name of "Essenflour Products Limited", an undertaking has been started in Mysore, India, with a capital of 200 000 rupees, for the purpose of producing oils of cinnamon leaves, cloves, coriander, dill, ginger, gingergrass, palmarosa, vetiver and musk grain[5]). The raw materials are found in Mysore and neighbourhood. Further perfumes like eugenol and geraniol are being produced. The erection of similar works for essential oils is contemplated also in Madras.

The Government of the United Provinces, India, announces that the industry of essential oils, the centre of which is at Kanauj, has done well in the last year. Attempts to distil oil of roses by means of new methods were not very successful. It is believed, however, that something will be attained by improving the quality of the flowers.

By means of a good distillation apparatus 4.5 per cent. of an oil of a high eugenol contents has been prepared from clove stems[6]). If a cheap raw material should become available, from Africa or some other country, the distillation of this oil was likewise to be taken up.

In a second article[7]) on *"Düfte im Mineralreich"* (Odours in the Mineral Kingdom) H. Heller[8]) discusses a paper by Brandt[9]), who likewise attempts to explain the smell phenomena in minerals and who has arrived at the same conclusions as Heller.

H. Schelenz[10]) also discusses the same subject and finds the answer to the question why minerals do not smell, in the thesis:—*"Corpora non agunt nisi soluta"*. Smelling

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[1]) *Deutsche Parf. Ztg.* 6 (1920), 244; translation from *L'Esportatore ed Importatore Italiano.* Cf. *Perfum. Record* 11 (1920), 354. — [2]) See also p. 32 of this *Report.* — [3]) Cf. *Report* November 1908, 100. — [4]) The translation speaks of *Siegwurz,* the rhizome of which is not utilised industrially. — [5]) *Perfum. Record* 11 (1920), 358, 386; also *Chemist and Druggist* 93 (1920), 1435. — [6]) Clove stems, which were distilled already about the middle of the XVIth century, yield in general 5 to 6 per cent. of essential oil. — [7]) Cf. *Report* 1920, 88. — [8]) *Deutsche Parf. Ztg.* 6 (1920), 245. — [9]) *Die Naturwissenschaften* 8 (1920), 689. — [10]) *Deutsche Parf. Ztg.* 6 (1920), 211.

substances must be dissolved, down to the gaseous state of aggregation, in fact, so as to be able to excite the cells of special conformation in the nose into which they penetrate and which cause the sensation of smell.

An apparatus for the *automatic separation of immiscible liquids,* especially of essential oils from aqueous distillates, is described by H. E. Watson[1]). The liquid is placed into a cylindrical vessel which is provided with a float fitted with a vertical rod. The rod passes through a hole in the lid and terminates at the bottom of the cylinder in a conical needle valve. Care must be taken to keep the weighted float in the interface between the two liquids and to introduce the distillate in the horizontal position. As soon as the level of the heavier liquid rises, the float is raised and the valve is opened. The liquid may then flow off, until the original level has once more been attained. The lighter liquid collects in the upper portion of the cylinder and is drawn off through a lateral tube. An apparatus of 8″ diameter and 10″ high can deal with 100 lb. of distillate per hour.

Bibliography.

R. T. Baker and H. G. Smith[2]) have published the second edition of their work *"A Research on the Eucalypts especially in regard to their Essential Oils"*, which first appeared in 1902. The republication and completion of this work, which is valuable not only for those interested in the subject, was as justified as necessary and will generally be welcomed, considering that the exploration of the species of eucalyptus and their oils and their utilisation in perfumery, medicine and the arts have seen many a novelty since the first publication of the work. In the present edition the original arrangement and division of the subject matter into a general, a botanical and a chemical part, with special regard to technics, have been maintained. New are the series of coloured illustrations examplifying the habitus of branches and flowers and cross and longitudinal sections of barks and leaves, which will be welcome to the botanist. The groups of the cognate eucalyptus species have been supplemented; altogether 176 different varieties are enumerated and are described in detail together with their oils. Since the species of eucalyptus of nearly all Australia and Tasmania have better been studied within the last 20 years—formerly the explored territory was confined to the south-east of the continent—the authors have also paid attention to the geographical distribution of the species and have elucidated by good maps, how the species are interconnected in geological, botanical and chemical respects. The chemical part which contains above all the results of their own experiments has been supplemented and amplified in every way. We might especially mention the chapters on piperitol and piperitone to which we have already alluded on page 23. A special chapter has also been devoted to the industrial utilisation of eucalyptus oils in which, among other things, the ore flotation process is discussed in detail.

The older methods for the determination of cineole are compared with one another, and their defects and advantages are discussed at some length. The view of the authors, that an accurate method applicable under all conditions has not yet been found and that, according to the quantity of cineole present, sometimes the one, and sometimes the other method would give better results, may be correct. We can, however, not quite agree with the opinion of the authors in favour of the modified

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[1]) *Journ. Soc. chem. Ind.* 40 (1921), A. 26. — [2]) Sydney 1920. We take this opportunity once more to thank the authors for obliging us with a copy.

phosphoric acid method and against the resorcinol method. We have sufficiently often explained our standpoint with respect to this question¹) and will refrain from raising the point again on this occasion.

A. Reclaire and F. Rochussen²) report on the *progress made in the domain of the chemistry of the terpenes and the essential oils* during the period 1916 to 1919.

Analytical Notes.

E. W. Dean and D. D. Stark³) describe a method for the *determination of water in petroleum and in other organic solvents* which might possibly find application in essential oils. The apparatus required consists of a flask with short neck which is joined to a reflux cooler by means of an elbow tube. At the end is a conical graduated cylinder into which the condensate drops directly. The sample to be examined is heated with the same amount (if necessary, with more) of a solvent which is not miscible with water, for example, a mixture of 80 per cent. xylene and 20 per cent. benzene. It is heated in such a way that two to four drops of distillate fall from the cooler per minute. The addition of the xylene-benzene mixture is to facilitate the suppression of any emulsion.

For the quantitative estimation of *highly volatile alcohols* A. Grün and Th. Wirth⁴) have worked out a method which is based upon the conversion of the alcohols into less volatile esters and upon the indirect titration of these esters. According to this method the substance to be analysed is made to react with the chloride of a higher aliphatic acid at a temperature below the boiling point of the alcohol, until the alcohol is quantitatively esterified. The excess of chloride is redecomposed again, by means of water, into free aliphatic acid and hydrochloric acid and washed out with water. The aliphatic acid having been neutralised, the ester is saponified and the percentage of alcohol is thereby determined. The authors recommend to take lauric, or lauric and myristic, acid chloride rather than palmitic or stearic chloride. In the analysis of most of the primary alcohols half an hour was sufficient for the reaction of the acid chloride. Geraniol and secondary alcohols, however, required longer periods of reaction (up to 3 hours), but they could then be determined with fair accuracy. Less good results were obtained with methylnonyl-carbinol. Secondary alcohols, the hydroxyl group of which is joined to a ring carbon atom (menthol), and tertiary alcohols of the type of linalool were found unsuitable for this method. The presence of acetone in the sample to be tested does not interfere with the accuracy of the method. In how far aldehydic mixtures are amenable to this treatment has not yet been ascertained by the authors.

Detailed experiments on the *solubility of vanillin and coumarin* in aqueous 5 to 50 per cent. glycerin solutions at different temperatures (0.2° to 60°) have been published by Melvin de Grote⁵). The author prepared saturated solutions of vanillin and coumarin and determined the quantities which had passed into solution by shaking the solutions (diluted with water) repeatedly with ether. In this extraction it must not be overlooked that glycerin, though insoluble in dry ether, is soluble in aqueous ether. For that

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¹) Cf. *Report* **1920**, 34. — ²) *Chem. Ztg.* **44** (1920), 853. — ³) *Journ. ind. eng. Chem.* **12** (1920), 486. — ⁴) *Zeitschr. d. Deutschen Öl- u. Fett-Ind.* **41** (1921), 145. — ⁵) *Americ. Perfumer* **15** (1920), 372.

reason the residue of the dry ethereal extract was a second time shaken with ether. We take the following figures from the solubility tables of the author[1]):—

100 parts of water dissolve at
0.2° 0.68 parts of vanillin and 0.09 parts of coumarin
20° 1.25 " " " " 0.11 " " "
60° 5.05 " " " " 0.70 " " "

100 parts of 50 per cent. glycerin dissolve at
0.2° 2.06 parts of vanillin and 0.287 parts of coumarin
20° 4.5 " " " " 0.50 " " "
60° 20.0 " " " " 2.20 " " "

As regards adulterations of coumarin, heliotropin and vanillin, cf. page 73 of this *Report*.

As regards the determination of chlorine in benzaldehyde, cf. page 53 of this *Report*.

As regards the testing of Peru balsam, cf. page 65 of this *Report*.

As regards the examination of civet, cf. page 60 of this *Report*.

Physical Notes.

On a previous occasion[2]) we had proposed the introduction of a standard pressure for the distillation at reduced pressures, also for the purpose of realising connection with the absolute system of measures. Of the pressures then discussed:—

10 kilobars = 10000 dynes/sq. cm. = 7.5 mm. of mercury, and
20 " = 20000 " " = 15.0 " " "

C. von Rechenberg[3]) selected the pressure of 15 mm. as normal pressure and he recalculates his well-known tables of boiling points on this basis. The lower pressure of 7.5 mm. is not to be recommended for experimental reasons[4]).

In this calculation use has only been made of the more exact determinations of the literature, as well as of a large number of supplementary figures which had been determined in our laboratory.

For those boiling points which had not been measured exactly at 15 mm. a correction is required which is based upon a formula of Crafts-Young:—

$$C = x(15 - p)(273 + t)$$

modified for this purpose, where C indicates the correction required for the boiling temperature observed at a pressure p, t is the approximately-estimated boiling point at 15 mm., and x is a coefficient which depends upon the nature of the material and which can be deduced from its vapour-pressure curve. According to the nature of the material definite groups may be distinguished in which the quantity x has an average value, applicable in order to correct other substances, of so-far unknown vapour-pressure curve, to pressures of 15 mm. These average values are:—

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[1]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 522. — [2]) *Report* **1919**, 95. — [3]) *Journ. f. prakt. Chem. N. F.* **101** (1920), 112. — [4]) Cf. C. von Rechenberg and E. Brauer, *Zeitschr. f. physik. Chem.* **95** (1920), 184.

0.004187	for	hydrocarbons, ethers, oxides, mustard oils, thiophenols, sulphides, nitriles, acid chlorides,
0.004009	„	ketones,
0.003946	„	esters, amines, aldehydes,
0.003720	„	phenols,
0.003574	„	acids,
0.003458	„	alcohols,
0.00301	„	hydrazones,
0.002835	„	quinones.

H. Offermann[1] has published a method of *distillation* claimed to be new for the estimation of the single fraction of highest value in petroleums and their residues, and in general in oils which are not miscible with water, in fats, resins, tars &c. The method is based upon the introduction of "cold" steam (100° and less) into the boiling substance under distillation. The author believes that he can dispense with a vacuum in the cautious distillation of sensitive substances. Since we cannot distil, however, by the aid of liquid water, even when it is introduced in the shape of drops, the heat which the distillation necessitates must externally be applied. In the most favourable case, therefore, this method would be the well-known water distillation, the sparing character of which has long been understood. A new idea can certainly not be discovered in the utilisation of saturated steam.

In the course of a research on the substance, in crude acroleïn, which stabilises acraldehyde Ch. Moureu, Ch. Dufraisse and P. Robin[2] have made use of the method of repeated fractionated distillations at exactly the same pressure, uniting always such fractions with one another which were equal, not only as to boiling point, but also as to density and refractive index, and submitting these again to fractionation. It may expressly be stated for the reader not acquainted with the principles of the theory of vapour pressures[3], that this method will yield not only uniform substances in pure condition, but also mixtures in definite proportions of substances of two or more constituents.

When the distillation is conducted at reduced pressure, this pressure has to be kept constant throughout. In the opinion of the authors this is better secured by means of their differential manometer of vaseline oil, which they illustrate in their paper, than by the aid of a mercury manometer. The former manometer is said to be 15 times more accurate and sensitive than the ordinary vapour-pressure gauges.

H. C. Wood Jr.[4] has determined the *solubility* of some *essential oils in mixtures of alcohol and water.* The method of which he makes use resembles in principle that recommended by Dowzard[5] (addition of water to a concentrated solution of the oil in 93 per cent. alcohol to incipient turbidity). Wood himself admits that this method, which so far has only rarely been applied, is subject to errors.

None of the oils examined by the author gave a clear solution with 100 parts of 55 per cent. alcohol. At a certain point, however, the solubility of the oil decreased markedly with slight changes in the concentration. This "critical point" of Wood was near 60 per cent. for clove oil, and near 90 per cent. for peppermint oil[6]. In general most of the essential oils were not readily-soluble in 70 per cent. alcohol.

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[1] *Chem. Ztg.* **44** (1920), 773. — [2] *Compt. rend.* **169** (1919), 1068; *Bull. Soc. chim.* IV. **27** (1920), 523. — [3] Ostwald, *Lehrbuch der allgemeinen Chemie*, 2nd ed., vol. II, 2: *Verwandtschaftslehre, zweiter Teil*, p. 992; v. Rechenberg, *Gewinnung und Trennung der ätherischen Öle*, p. 572. — [4] *Journ. Americ. pharm. Assoc.* **9** (1920), 878. — [5] Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 568. — [6] Further information as to the interpretation of these figures is not given.

We should particularly point to the behaviour of clove oil and of eugenol. Although the clove oil used contained 82 per cent. of eugenol, the solubility of these two products was strikingly different (compare table below). The case exemplifed how much very slight variations in the composition of essential oils can influence their properties. The table is a summary of the results of Wood's experiments:—

Per cent. alcohol	Solubility in 100 parts of alcohol at different concentrations					
	Oil of anise	Cinnamon	Cloves	Eugenol	Peppermint	Sassafras
30 p. c.	0.05	—	0.02	—	0.02	0.07
40 p. c.	0.08	—	0.10	0.30	0.02	0.10
50 p. c.	0.10	0.20	0.40	5.80	0.03	0.20
60 p. c.	0.25	0.40	2.00	16.00	0.06	1.30
65 p. c.	0.80	1.10	10.00	—	0.07	2.3
70 p. c.	1.50	2.20	21.75	—	0.10	4.00
75 p. c.	4.00	7.00	—	—	0.17	7.00
80 p. c.	7.50	—	—	—	0.35	11.00

In an extensive paper F. Eisenlohr and E. Wöhlisch[1]) show with reference to some 400 compounds, taken from the literature, that the *molecular coefficient of refraction*, that is, the product of refractive index and molecular weight, represents a valuable supplement to the molecular refraction and dispersion, particularly in researches on the constitution. From the normal series of the paraffins, primary alcohols, aldehydes, ketones, acids and esters he deduced the mean fundamental value of the molecular index of refraction $M \times n_{D20^{\circ}}$ for the methylenic group, the constant $CH_2 = 20.56$. The influence of the ethylene-bond $[/^{=} = -6.7]$, and of hydrogen $[H = -4.99]$ appeared as a negative quantity (decrement). The highest value would then be attached to oxygen in its saturated bonding, the hydroxyl oxygen $[O^{\cdot} = 26.54]$, the lowest value to the double-bonded carbonyl oxygen [$O^{\cdot\cdot}$ (in ketones) = 16.98]. The limit of error for the expression $M \times n_{D20^{\circ}}$ is 0.2 unit. Eisenlohr considers that the molecular coefficient of refraction furnishes a simple and reliable means of testing a liquid compound for its purity.

The study of the influences which the constitution of the compounds has upon the product $M \times n_{D20^{\circ}}$ led to the following general results:—In acyclic compounds the entry of a side-chain into a position next to the carbon atom at the end of a chain decreased the value of the molecular coefficient of refraction by 0.2 unit with respect to the value calculated from the equivalent. On the other hand, the entry of a side-chain into a position further removed from the extreme carbon atom raised its value by 0.45 unit. In cyclic, non-aromatic bodies distinct influences were noticed of the different cyclical linking, the decrements increasing steadily from the 8-member-ring to the 3-member-ring. The entry of a side-chain caused, by contrast to the acyclic compounds, a further diminution of the value $M \times n_{D20^{\circ}}$ (increase of the depression). Homologues differed from one another according to the mutual position of the side-chain and the double linking.

The aliphatic acids and esters occupied in so far a special position, as the observed values for the molecular coefficient of refraction were found to be lower by 2.23 to 2.65 units than the calculated values. Since now the ring-formation always introduced a specific decrement, the authors assume that acids, like esters, form a kind of ring owing to some accessory binding.

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[1]) *Berl. Berichte* 53 (1920), 1746.

In a further paper Eisenlohr[1]) reports on the precalculation of the index of refraction in the case of aromatic hydrocarbons. The values for the expression $M \times n_{D20^\circ}$ showed, in the case of the benzene hydrocarbons, a number of regularities, the enumeration of which would carry us too far. These intimate relations between the observed and the calculated molecular index of refraction admit, with the help of the "E" value of any compound (excess, positive or negative, resulting for the expression $M \times n_{D20^\circ}$ with regard to the sum of the constants for branch chains and for rings), of calculating the "E" value and hence the refractive index for any other aromatic hydrocarbon. The introduction of side-chains into the benzene ring led to excesses, the amount of which depended upon the number and the mutual positions of the substituents. The neutral conjugation of the three ethylene bonds in the benzene nucleus (Brühl) was eliminated by the entry of side chains, and the now starting conjugation-effect of the ethylene linkage gave the excesses. Such conjugation effects were in general indicated in the expression of the molecular coefficient of refraction by the excess of the observed values over the calculated figures. The inter-relations, established for benzene hydrocarbons, between the molecular coefficient of refraction and the constitution do not represent any special case, limited to this class of substances. In other cases, however, as, for instance, with the cyclohexanes, the observed values extant were not always sufficiently reliable.

W. Deutschmann[2]) has investigated the deviations of the *optical rotation* from the law of Biot, according to which the specific rotation of an active substance is the same for all concentrations and for all solvents (molecular rotation). He finds that these deviations can be traced back to the formation of compounds between the solute and the solvent, or to changes in the degree of association.

In order to determine the *diamagnetism* of *solid odorous substances* H. Zwaardemaker and F. Hogewind[3]) incorporated these materials by spraying them into paraffin of known diamagnetic susceptibility. Their diamagnetism could then be compared with the diamagnetism of the liquid substance or its solution in water. The values found for the solid substances corresponded to those previously observed for the liquid materials.

Botanical Notes.

In a communication on the production of *medicinally-valuable species of plants* by selection W. G. Smith[4]) points out that the breeding of plants, important in agriculture, has made more progress than the cultivation of medicinal plants. Whilst the agricultural cultivation was being promoted by the governments and larger public bodies, which publish their results, the nursing of medicinal plants was mostly in private hands which keep their experience and methods to themselves.

Larger specimens could be obtained by suitable manuring and careful attention to the plants, but properties like the quality and the proportion of the efficient constituents could only be influenced by selective breeding. Qualitative changes could already be attained by mass selection, by mixing a number of selected specimens with the more common kinds. The best results were, however, realised by selecting superior specimens and by propagating from them in true breeding. The hybrids are particularly

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[1]) *Berl. Berichte* **53** (1920), 2053. — [2]) *Zeitschr. f. physik. Chem.* **95** (1920), 385. — [3]) *Archives néerland. d. Phys. de l'homme et des animaux* 4 (1920), 224. From *Chem. Zentralbl.* **1920**, IV. 507. — [4]) *Perfum. Record* **11** (1920), 144.

valuable for the plant breeder since he can, by cross breeding of different varieties, obtain novelties and improvements in any desired direction.

In France the best species of lavender are under cultivation, and the oils obtained from *Lavandula vera fragrans* and *L. vera delphiniensis* surpass all the products of other lavender species growing in France, by their superior character[1]. Both the varieties thrive in the subalpine region at an elevation of more than 1300 feet in the south east of the country. The *Lavandula spica*, D.C. which like the hybrid of *Lavandula vera* and *spica* gives a less good oil, mainly utilised in varnishes, grows at lesser altitudes. The special properties of the English oil of lavender are likewise due to the long-continued cultivation of the plant by a few breeders.

Beautiful success has been obtained in Hungary with peppermint which has systematically been cultivated there since 1904 and has been improved by selective breeding. One of the most successful early pioneers in this field was Father Joseph Agnelli, who produced the "Agnelliana" varieties of *Mentha crispa* and *Mentha piperita*.

The fact that *Mentha* species incline to hybrid formation may account for the manifold variations of peppermint. One kind is known as red peppermint in France where it is becoming more and more popular according to Smith; it grows on soil which would be unsuitable for *Mentha piperita*, L. The red peppermint, moreover, may be grown for four or five years in succession on the same plot, whilst *Mentha piperita*, L. only thrives two consecutive years on the same field. The yield of oil is greater with the former species than with the latter; the product itself, however, is inferior.

From the *Deutsche Parfümerie-Zeitung*[2] we take a few statements on the fight against insect-pests, acquaintance with which may be valuable also for the cultivation of aromatic plants. The Schweinfurt green (aceto-*meta*-arsenite of copper), with which the Colorado beetle was fought between 1860 and 70. in the United States of North America, is a well-known general remedy against insect-pests. In Germany this poisonous preparation, as well as Urania green and lead arsenite *(Zabulone)* were only used during the War when the nicotine formerly applied disappeared almost completely from the market. According to Stellwaag[3] the fight against insects by means of these arsenites is hygienically free of objection, provided the spraying be stopped 5 weeks before the harvest. On the other hand the *Biologische Reichsanstalt* and the *Reichsgesundheitsamt* have pointed out that grape-juice and wine may be poisoned when the vines are sprayed with arsenious chemicals. A non-poisonous spray, recommended under the name of "resinol" by the Chemical Works of F. Raschig, is the alkali or alkaline earth salt, soluble in water, of an artificial phenolaldehyde resin. It has been applied with success by R. Falck[4] against the caterpillar of the common white cabbage butterfly. Very good results have been realised in this fight against insects by means of gases or volatile liquids like sulphur dioxide, prussic acid and esters of the cyanocarbonic acid mixed with esters of the chlorocarbonic acid (known in mixtures under the name of "Zyklone"). Whilst we are not sure, when using substances suspended in water or dissolved in water, that all the parts of the plant will be struck, the gases penetrate everywhere and destroy all small life. On the other hand it is difficult to secure efficient action of the gases in the open field. It is not stated how this difficulty is overcome.

The *animal pests of plants* may, according to F. Zacher[5], be divided into two groups:—1. the oligophagi, which attack only a few species of plants related to one

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[1] Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 421. — [2] *Deutsche Parf. Ztg.* 7 (1921), 16. — [3] *Zeitschr. f. angew. Entomologie* 7 (1920), 172. — [4] *Ibidem* 7 (1920), 37. — [5] *Berichte d. deutsch. pharm. Ges.* 31 (1921), 53; reprint was kindly sent to us.

another, and 2. the pœcilophagi, which attack many plants of the most diversified families. To the second group belong among others the insects of the soil, such as mole crickets, the larvæ of cockchafers and wire-worms which eat almost anything that their jaws are able to deal with.

In agreement with other authors[1]) Zacher accentuates that much injury to plants may be evaded by providing in the cultivation for the best possible conditions. This is all the more important, because just the cultivated plants which are crowded in a narrow space, offer good opportunities for the propagation of the insects and are hence more exposed to their attacks than the wild-growing plants.

Of the examples quoted by the author *Valeriana* and *Mentha* are of special interest for us. Valerian is relatively disliked by insects. Its leaves are eaten by four caterpillars of butterflies, *viz.* the caterpillar of the *Melithœa dictynna,* S., which is provided with spikes, the caterpillar of a moth (*Caradrina quadripunctata,* F.), a "looping" caterpillar (*Tephroclystia valerianata,* Hb.) and the caterpillar of a small butterfly (*Depressaria pulcherimella,* Stt.). A gall mite (*Eriophyes macrotuberculatus,* Nal.) causes the flowers to turn green, whilst the development of the axis of the inflorescence is prevented by the larvæ of the gall-gnat (*Contarinia valerianœ,* Rübs.); the flowers are then crowded and remain barren. In the stalk of the mint lives the larva of a beetle with a sorex trunk (*Apion vicinum,* Kby.) and causes an oval or coniform swelling, more or less red in colour, above one of the upper knots. The leaves are eaten by two leaf flees (*Longitarsus Waterhousei,* Kutsch. and *lycopi,* Foudr.) and also very largely by the beautiful big blue beetles of the species *Chrysomela cœrulans,* Scriba, and their variety, *Menthastri,* Suffr., which are often of a golden lustre. On *Mentha* we further find the prickly mud-covered larvæ of two bugs (*Cassida viridis,* L. and *Murrœa,* L.). In addition quite a dozen of butterfly caterpillars, the enumeration of which would lead us too far, feed on the mint. In the swollen buds which then remain closed is found the ochre-yellow larva of a gall-gnat (*Asphondilia menthœ,* Pierre). Two gall-gnat species produce galls in sprouts and leaves.

Phytophysiological Notes.

According to all experience the essential oils are by-products and final products of the plant assimilation. As regards their mode of formation it is only known that they are formed like the balsams and resins, partly in the interior of the protoplast, subsequently to coalesce to homogeneous masses of oil and balsam, or to remain in a state emulsion as in milk saps. The plants, however, also secrete substances which outside the protoplast are either converted into essential oils or balsams, or which take their origin from a metamorphosis of the cell membrane[2]). Frequently the essential oil of the living cell is changed by exposure to the air, as, for instance, in the camphor tree where it is converted into camphor by post-mortal absorption of oxygen.

As regards the ecological importance of essential oils, that is, their importance in the external life of the plant, we take a few statements from an article by N. Patschowsky[3]). Whilst the oils of agreeable scent, present in the petals, allure insects chiefly for asphyxiation, the essential oils present in the vegetation-organs of the plant are credited with various other tasks. Some authors presume that the essential oils, which are formed in the epidermal glands of the plants, are to protect them against overheating and excessive transpiration. More probable than this somewhat dubious hypothesis is the view that the odorous substances are able to keep deleterious organisms at a distance.

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[1]) *Report* 1920, 107. — [2]) Pfeffer, *Pflanzenphysiologie.* 2nd ed., vol. I, p. 501. — [3]) *Naturw. Wochenschr.* **1920**, 497; from *Naturw. Umschau d. Chem. Ztg.* **9** (1920), 134.

It has been demonstrated by experiments that carrots which had gently been brushed with leaves of different labiates, geranium species or garden rue, are not touched by animals.

We should mention here further that essential oils can also serve, at least indirectly for the protection of wounds and for the prevention of undesirable loss of moisture[1].

After M. Greshoff[2] had demonstrated some years ago that the common fern, *Pteris Aquilina*, L., contains a *glucoside* which *carries prussic acid*, M. Mirande[3] has recently made a similar observation on a fern which is frequently found in the mountains of Savoy and in the Dauphiné, *Cystopteris alpina*, Desv. (*Cystopteris fragilis*, Bernh., *var. alpina*, Koch). The glucoside, which belongs to the amygdalin group and is contained in the fresh green parts of this fern, liberates already in drying or when the leaves wither prussic acid and benzaldehyde, in addition to other products. The quantity of glucoside initially present in the leaves diminishes gradually in the course of the season.

Physiological and Pharmacological Notes.

In an article on *odour* and *residual affinities*, Th. H. Durrans[4] further discusses his theory of smell to which we have already alluded[5]. We summarise once more the main points of the theory of Durrans without going into the detail of the examples which are no langer new.

According to Durrans an odoriferous substance must (1) have residual affinities, (2) be soluble in water and in the lipoid fats of the nose and must satisfy certain other physiological conditions[6], and (3) be volatile.

Not only the smell as such, but also the intensity of the smell will depend upon these three conditions. If one of them be unfulfilled, the consequence may be absence of odour.

Many facts support this theory of residual affinity. Bodies of similar type and similar structure often have cognate odours. If the residual affinity be suppressed in a molecule, its odour will be changed. This is observed among other things in the reduction of ketenes to ketones and in the comparison between unsaturated bodies and the corresponding saturated compounds. The position and distribution of the residual affinities likewise plays an important part. The symmetrical diphenyl ethylene has a strong floral scent, whilst 1:1-diphenyl ethylene smells only faintly. Elements which possess residual affinities, like oxygen, nitrogen, sulphur, phosphorus and the halogens, form strongly-osmophoric groups; carbon and hydrogen, the affinities of which are fixed according to Durrans (?)[7], do not. The osmophoric elements are also near one another in the periodic table. When in an odorous compound the atoms of partial valency are replaced by others, which do not possess any residual affinity, the odour disappears likewise. From cacodyl would thus result the odourless ethane, from methyl iodide methane.

We take the following statements of interest for our special domain from a paper, published by the German Board of Health written by E. Hailer, *"Vergleichende Versuche über die Einwirkung chemischer Mittel auf Kleiderläuse"* (Comparative Experiments on the Action of Chemical Reagents on Clothes-Lice)[8].

Some 200 compounds of all classes of substances were tested as to the rapidity and permanency of their action on lice. Thymol is among the substances which take

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[1] We should in this connection refer again to Oliver's theory of resin-formation, see p. 45 of this *Report*. — [2] *Report* November **1908**, 162. — [3] *Compt. rend.* **167** (1918), 695. — [4] *Perfum. Record* **11** (1920), 391. — [5] *Report* **1919**, 107. — [6] No details given. — [7] But carbon is not always credited with the same valency. — [8] *Arbeiten aus dem Reichsges.-Amt* **52** (1920), 312, 328.

some time to acquire a fatal vapour concentration, but with which the effects then persist for longer periods; possibly also ethyl benzoate. Many aromatic and aliphatic hydrocarbons, as well as phenols, salicylaldehyde, eucalyptole and *cyclo*hexane, act quickly asphyxiating; but they lose their efficiency already with weak aeration. Eugenol is one of the remedies which act quickly and which retain their effect for a long time, even with strong aeration. Of the esters of aliphatic acids, ethyl formate is especially effective. On the other hand, there is among the esters of the aromatic acids not a single one which approaches these compounds in their asphyxiating power. Relatively most favourable are ethyl benzoate and methyl salicylate (wintergreen oil). Among the hydroaromatic substances and terpenes, none were found which, applied in small proportions, asphyxiated or killed the lice at once. The effects of compounds of this group were very heterogeneous like those of the essential oils. It is noteworthy that eucalyptole killed lice after 30 minutes and that pinene, carvene and thymene, but not camphene, had a relatively-strong influence. Of terpene alcohols linalool was alone active; of aldehydes and ketones, citronellal, citral, and carvone and fenchone were moderately effective. *Cyclo*hexane and phenyl mustard oil (phenylethyl mustard oil?) proved somewhat stronger. The oils of anise, eucalyptus, fennel, origanum, turpentine, peppermint and wintergreen oil killed the lice within 60 to 120 minutes.

The volatile oils have a relaxing effect upon plain muscles, inhibiting their movements. According to J. W. C. Gunn[1]) this phenomenon would explain the carminative action of these oils. The other effects of the essential oils upon the gastro-internal tract are explained by local irritation and the reflexes arising from it, possibly also by acceleration of the absorption.

Ketocineole.—According to G. Cusmano[2]), ketocineole, contrary to camphor which it resembles in its constitution, does not stimulate the central nervous system, but causes a depression of the cerebral activity. Especially in the experiments made with frogs the initial action of camphor, reminding of curare, was missing in the case of ketocineole.

A. Fuchs[3]) has injected supersan (menthol-eucalyptol mixture)[4]) in about 200 cases of influenza, once or twice daily, in doses of one or two cc., intramuscularly. He observed a very favourable influence upon the bronchial-catarrh phenomena (facilitated secretion, copious phlegm), especially with early application of the remedy.

As regards the use of *benzyl alcohol* for curing toothache, compare p. 52 of this *Report*.

As regards the use of *benzyl benzoate* in medicine, cf. p. 52 of this *Report*.

As regards the use of *camphor* in medicine, cf. p. 59 of this *Report*.

With respect to *oil of peppermint* as remedy against cholelithiasis, cf. p. 33 of this *Report*.

As regards poisonous symptoms caused by the partaking of *oil of turpentine*, cf. p. 48 of this *Report*.

With respect to injections of the *ethyl* and *methyl ethers* of *thymol*, cf. p. 72 of this *Report*.

As regards the use of *cinnamic aldehyde* in the treatment of *lupus* and *scrofulous glands*, cf. p. 60 of this *Report*.

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[1]) *Journ. Pharm. and exp. Therapeutics* **16** (1920), 39; from *Chem. Zentralbl.* **1920**, III. 804. — [2]) *Gazz. chim. ital.* **49** (1919), II. 228; from *Chem. Zentralbl.* **1920**, III. 259. — [3]) *Münch. med. Wochenschr.* **1920**, 1018; from *Therap. Halbmonatsh.* **34** (1920), 610. — [4]) *Report* April **1915**, 77.

Chemical Notes.

Unsaturated compounds like geraniolene, *cyclo*geraniolene, menthene, and oils like oil of turpentine and lemon oil, can serve as catalysts in the oxidation of other bodies. J. Bougault and P. Robin[1]) obtained from a solution of dichlorodiethyl sulphide (mustard gas) in such an unsaturated compound, in the presence of oxygen, quantitatively dichloroethyl sulphoxide. This catalytic oxidation is possible only with substances which will dissolve in the catalyst and the oxidation product of which is insoluble in it. Thus thiodiglycol, which is insoluble in hydrocarbons and in oils, could not be oxidised to thiodiglycolsulphoxide, but was slowly oxidised when dissolved in citral. The reactions indicate that unsaturated compounds play an important part also in the physiology of the living organism.

The investigation of the *mercury derivatives* of *ethylene* had led W. Manchot[2]) to the conclusion that these bodies are not to be regarded as mercurated ethanoles $CH_2OH{-}CH_2HgX$, but as additive ethylene compounds of the constitution $C_2H_4Hg\langle^{OH}_{X}$. In order further to investigate substituted ethylenes (benzene derivatives with an unsaturated side chain) in this respect Manchot, F. Bössenecker and F. Mährlein[3]) mercurated safrôle and eugenol methyl ether each with one molecule of mercuric acetate in acid solution. The addition of sodium chloride produced well-defined additive compounds of the constitution $H_2C\langle^{O}_{O}\rangle C_6H_3 \cdot CH_2 \cdot CH{=}CH_2 \cdot Hg\langle^{OH}_{Cl}$ (monoclinic prisms, m. p. 136 to 137°) and $C_6H_3(OCH_3)_2{-}CH_2{-}CH{=}CH_2 \cdot Hg\langle^{OH}_{Cl}$ (white needles, m. p. 112.5°). In a similar way the authors prepared the corresponding bromide $C_{10}H_{10}O_2Hg\langle^{OH}_{Br}$ (white needles, m. p. 144 to 145°) and iodide $C_{10}H_{10}O_2Hg\langle^{OH}_{I}$ (shining needles, m. p. 152.5°) of safrole. All these safrole and eugenol methylether derivatives held mercury in strong union.

Safrole heated with 3 molecules of mercuric acetate in aqueous solution took up another atom of mercury and formed a product of the composition $C_{10}H_{10}O_2 \cdot HgO \cdot HgCl_2$, which was, however, insoluble and difficult to obtain in the pure condition.

Contrary to its methylether, eugenol did, in mercuration with 1 molecule of mercuric acetate, not give a well-defined product; with 3 molecules of mercury salt it gave, on the other hand, like safrole a derivative, difficult to purify, richer in mercury. Styrenes, having the methylated side chain in the end position, like *iso*safrole, $H_2C{=}O_2{:}C_6H_3{-}CH{=}CH \cdot CH_3$, and *iso*eugenol $(HO)(CH_3O(C_6H_3{-}CH{=}CH \cdot CH_3$, behaved differently in so far as they reduced the mercury salt when treated in the same way as safrole. Styrene itself (phenylethylene) yielded compounds, rich in mercury, but easily decomposible, the mercury of which was already split off by treatment with caustic soda.

In a further paper[4]) Manchot and Bössenecker deal with the mercuration of phenolethers. Even with an excess of mercury salt cresolmethylether, anisole and phenetole took up only one atom of mercury. Since the compositions of the products thus obtained distinctly deviate from those calculated for nuclear mercury compounds, the substances are regarded as additive products. As, moreover, the mercury component

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[1]) *Compt. rend.* 171 (1920), 353. — [2]) *Liebig's Annalen* 420 (1920), 170. — [3]) *Liebig's Annalen* 421 (1920), 316. — [4]) *Liebig's Annalen* 421 (1920), 331.

added may be hydrolysed to different degrees in different cases, it is intelligible why these products do not show exactly analogous compositions.

The treatment of anisole with mercuric acetate led, in two experiments, to two preparations of melting points 173° and 169°, based upon the formula $(C_7H_8O \cdot HgOH)OH$. The difference of the melting points is ascribed by the authors to the circumstance that a little water was split off in the one case. Hot solution of sodium chloride yielded from the mercury derivative the *p*-anisylmercuric chloride $CH_3OC_6H_4HgCl$ (m. p. 236 to 237°) which is mercurated in the nucleus. This body was identical with the substances prepared by Michaelis and Rabinerson[1] and by Dimroth[2].

Analogously an additive product of hydrated mercuric oxide and phenetole $(C_2H_5OC_6 \cdot H_5 \cdot HgOH)OH$ (m. p. 135.5°) and a *p*-phenetylmercuric bromide $C_2H_5OC_6H_4HgBr$ (m. p. 238°) mercurated in the nucleus, were obtained.

Hydrocarbons.

Heptane.—E. and R. E. Kremers[3] have commenced publication of an investigation of the chemistry of heptane and heptane solutions. Whilst 25 years ago the physical chemists of the school of Ostwald had only known a chemistry of aqueous solutions, the authors had always desired to study also non-aqueous solutions. The behaviour of a group of isomeric nitrosochlorides—of true, simple nitrosochlorides, *iso*nitrosochlorides and bis-nitrosochlorides—and also of cognate compounds in various organic solvents had already in those days pointed to the importance of the chemistry of non-aqueous solutions. Heptane had the advantage over other organic solvents that it is a volatile, saturated hydrocarbon, the boiling point of which comes very near that of water.

These authors have now succeeded in preparing perfectly pure *n*-heptane[4] from larger quantities of balsam oil of *Pinus sabiniana,* Douglas. By steam distillation the crude product yielded 4.2 to 9.4 per cent. of an oil which already had the properties of an exceptionally-pure heptane. It was in spite of this appearance further purified by means of concentrated sulphuric acid and of 1 per cent. solution of permanganate and by repeated fractionation. The heptane thus purified had the following constants:—b. p. 97.33° (760 mm); d_{20° 0.68288; d_{40° 0.66623; $[\alpha]_D \pm 0$; n_{D20° 1.3895.

In a further paper E. Kremers and D. C. L. Sherk[5] report upon the preparation and the properties of saturated solutions of hydrohalogens in heptane. Hydrogen fluoride was soluble to about 0.05 per cent., the chloride to 0.622 per cent., the bromide to 3.57 per cent. and the iodide to 15.31 per cent., in the hydrocarbon at 20 per cent. They studied the action of these solutions upon a series of metals and they ascertained that some of these elements are soluble in the liquids, partly under generation of hydrogen.

p-*Cymene.*—Spruce turpentine oil, which is obtained from the spruce fir as a by-product in the paper manufacture by the sulphite-pulp process, consists very largely of *p*-cymene. A. S. Wheeler[6] prepared the latter in the pure state by first passing a current of air through the crude material for some time, thus removing the sulphur dioxide. The oil was then distilled by means of superheated steam. The vapours were sent first through a 30 per cent. solution of sodic hydrate before they were col-

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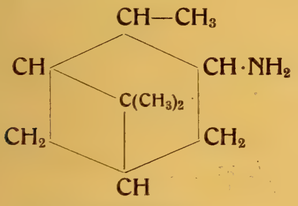
[1] *Berl. Berichte* **23** (1890), 2344. — [2] *Berl. Berichte* **35** (1902), 2867. — [3] *Journ. Americ. pharm. Assoc.* **9** (1920), 857. — [4] The distillate, which Thorpe obtained from *Pinus sabiniana,* showed a feeble rotation and could hence not be pure heptane.—Years ago we obtained a distillation product the main fraction of which was optically-inactive; see *Report* October **1906**, 64 and also April **1913**, 102. — [5] *Journ. Americ. pharm. Assoc.* **10** (1921), 26. — [6] *Journ. Americ. chem. Soc.* **42** (1920), 1842.

lected in the cooler. After treating the distillate with 5 per cent. soda lye it was once more distilled over metallic sodium. The *p*-cymene obtained in this way had the following constants:—b. p. 176 to 176.5°; $n_{D12.5^\circ}$ 1.4905.

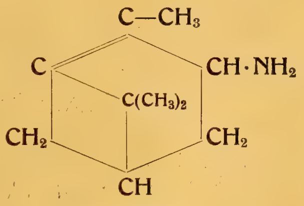
Since purified *p*-cymene is an important solvent Wheeler determined the solubility of some compounds in this substance at different temperatures: 100 g. of *p*-cymene dissolved 1.53 g. of *d*-camphoric acid at 100°, 113.85 g. of thymol, 6.53 g. of benzoic acid and 0.986 g. of salicylic acid at 25°.

The author observed further that *p*-cymene was quickly coloured red by an addition 0.2 per cent. of *p*-anisidine. Other impurities cause similar colorations, whilst the pure *p*-cymene remains colourless.

Pinene.—A new partial synthesis of pinene *via* the pinocamphyltrimethylammonium hydroxide, yielding a pure pinene of b. p. 156° (725 mm.), has been effected by L. Ruzicka and H. Trebler[1]. They started from pinocamphylamine (I) which was prepared by the catalytic reduction of pinylamine (II); the further synthesis proceeded along the line of the reactions which we describe in the case of bornylene (see page 103 of this *Report*). The authors could also in this case prepare two isomeric pinocamphyltrimethylammonium iodides (m. p. 255° and 300 to 301°). In preparing the pinenenitrosochloride the authors observed, that alcoholic hydrochloric acid yields a product of a higher melting point, 107 to 108°, than that which results when the process of Wallach is employed (m. p. 103°).



(I) Pinocamphylamine.



(II) Pinylamine.

Ruzicka and Trebler further report on experiments which were partly failures, undertaken to prepare, from pinonic acid (III), the easily-accessible oxidation product of pinene, the homopinocamphoric acid which was not known so far. In this the authors made the following observations:—

(1) The ethylpinolate (IV) prepared by catalytic reduction of ethylpinonate yielded with phosphorus pentachloride, in addition to pinocampholenic ester, only little of the desired chloroester (V). They did not succeed in converting this ester into homopinocamphoric acid. In the preparation of ethylpinonate (b. p. about 100° [one third mm.], semicarbazone m. p. 136°) it was noticed that pinonic acid was, under certain conditions, easily esterified already by very weak alcoholic hydrochloric acid.

(2) In treating the ethylester of pinonic acid cyanohydrin with phosphorus pentachloride they did not obtain the expected ester of dehydrohomopinocamphoric nitrile acid, but the aliphatic 2-cyano-6-methyl-2 : 6-heptadiene-5-acetic acid ethylester (VI) which, on saponification, yielded the dicarboxylic acid of constitution (VII). From the latter they obtained, by treatment with acetic acid anhydride in a sealed tube, the intermediary anhydride (VIII) and further the unstable ketone (IX) and carvacrol (X). This reaction represents a new mode of preparing this phenol. By reduction and

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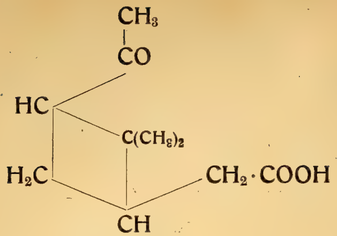
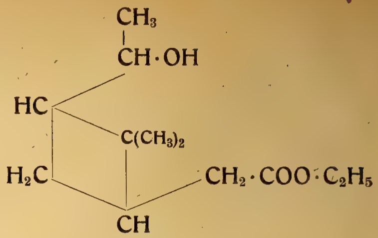
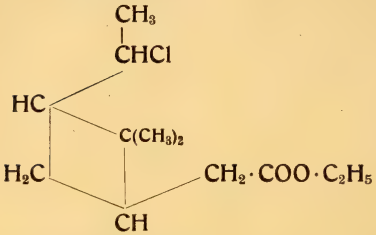
[1] *Helvet. chim. acta* 3 (1920), 756.



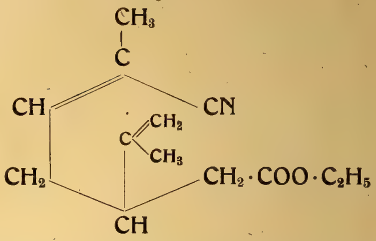
(III) Pinonic acid.



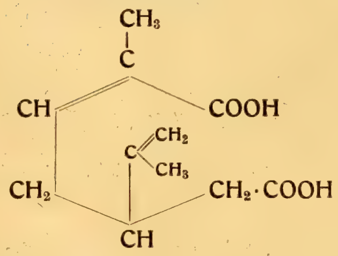
(IV) Ethylpinolate.



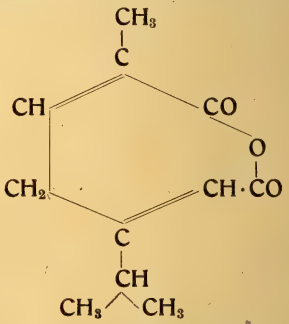
(V) Ethylchloropinolate.



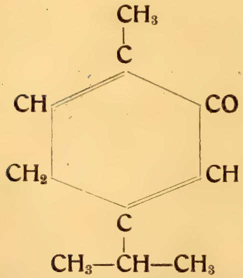
(VI) 2-Cyano-6-methyl-2:6-heptadiene-5-acetic acid ethyl ester.



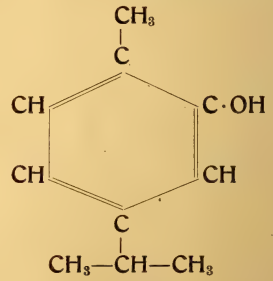
(VII) Dicarboxylic acid from VI.



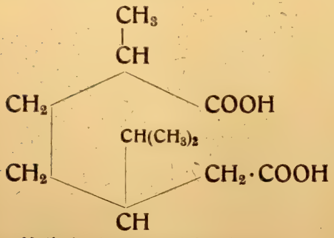
(VIII) Anhydride of transformed dicarboxylic acid (VII).



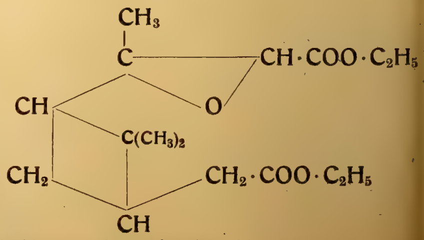
(IX) Unstable ketone passing into carvacrol.



(X) Carvacrol.



(XI) α-Methyl-β'-*iso*propylpimelic acid.



(XII) Glycide ester from pinonic acid ester.

subsequent saponification of the unsaturated dicarboxylic acid they further prepared the α-methyl-β'-*iso*propylpimelic acid (XI), an amorphous, viscous mass and from this, by distillation of its lead salt or by condensation of the ester with sodium, tetrahydrocarvone (m. p. 90° [11 mm.]) as only product. It would therefore appear, in confirmation of Wallach's[1] researches, that the derivatives of pinene and pinonic acid, having a double bond semicyclically attached to the four-member-ring, are scarcely stable, and that they become stabilised by an intramolecular rearrangement or ring-scission.

(3) From the chloroacetic ester and the ester of pinonic acid the glycide ester of the formula (XII) was prepared in the presence of sodamide. The authors will later report on the further researches.

According to J. Schindelmeiser[2] the pyrogenesis of pinene yields, in addition to other products, in the gaseous portion propylene which was identified by its bromide (b. p. 141 to 143°, d_{15° 1.93; bromine percentage 80.47). The heating was effected in an electric furnace fitted with a wide silica tube which was loosely packed with fragments of porous silica.

Camphene.—The supposition that tricyclene (I) formed an intermediate product[3] of the conversion of *iso*borneol into camphene had recently been refuted by P. Lipp[4]. H. Meerwein and K. van Emster[5] come to the same conclusion. These authors maintain that under the conditions which effect an almost complete conversion of *iso*borneol into camphene—heating for several hours to 100° with 33 per cent. sulphuric acid—tricyclene is practically not affected at all. It was further demonstrated that the Tiffeneau's explanation[6], who suggests a compound with a bivalent carbon atom as intermediate product, is not applicable to these reactions. For the compound (II), which is produced by the action of mercuric oxide on camphor hydrazone and which is not capable of existence, was almost exclusively isomerised into tricyclene. An unsaturated hydrocarbon, probably camphene, was found only in a very small quantity.

$$C_8H_{14}\left<\begin{array}{l}CH_2\\ |\\ C:N:NH\cdot HgOH\end{array}\right. \longrightarrow C_8H_{14}\left<\begin{array}{l}CH_2\\ |\\ C<\end{array}\right. + N_2 + H_2O + Hg$$

Mercuric compound of camphor hydrazone. Not capable of existence.

That tricyclene cannot be an intermediate product of the *iso*borneol—camphene conversion was further proved by the inverted reaction—transformation of camphene into *iso*borneol or into its ester. For this purpose the authors compared the reaction velocities at which monochloroacetic acid unites with camphene and with tricyclene. This union leads to esters of *iso*borneol, as had long been known[7]. It was ascertained in this connection that the acid forms an additive compound with camphene much more rapidly than with tricyclene.

The authors further prove that the trimethylene-ring of tricyclene would appear to be most easily split, quite generally, between the carbon atoms 1:2 or 1:6. Thus tricyclene was, in the reduction with hydrogen and nickel, easily converted at 180 to 200° into *iso*camphane (III), the reduction being probably preceded by an isomeration of tricyclene into camphene. In any case tricyclene was quantitatively transformed into camphene when it was passed in a slow current of nitrogen over nickel at 180 to 200°.

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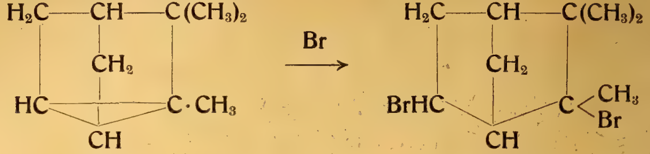
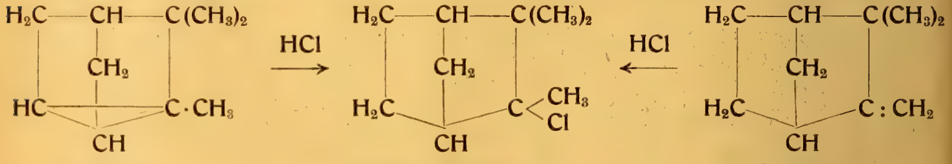
[1] *Liebig's Annalen* **360** (1909), 85. — [2] *Chem. Ztg.* **45** (1921), 7. — [3] Cf. *Report* **1919**, 115. — [4] Cf. *Report* **1920**, 129. — [5] *Berl. Berichte* **53** (1920), 1815. — [6] *Rev. gén. des sciences pures et appliquées* **18** (1907), 583. — [7] *Liebig's Annalen* **340** (1905), 25.

The fairly-rapid formation of an additive compound between bromine and tricyclene led to a liquid dibromide[1]), possibly according to the following scheme:—

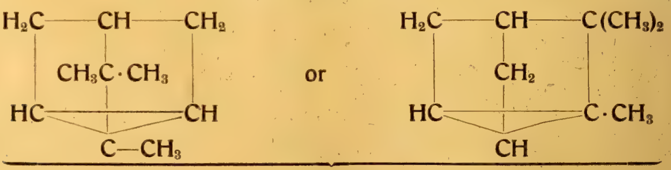


Tricyclene. Tricyclene dibromide (?) (constitution not yet certain).

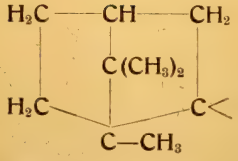
A complete elucidation of the above-mentioned transformation was obtained by the treatment of tricyclene and of camphene with gaseous hydrochloric acid. Both these compounds yielded then the true, so far unknown, camphene hydrochloride (m. p. 125 to 127°), the chloride of Aschan's camphene hydrate[2]). The camphene hydrochloride is, as a tertiary chloride, characterised by the high mobility of the chlorine atom and by the ease with which hydrochloric acid is split off and camphene is formed. The low stability of the chloride is connected with this fact. In storing, the hydrochloric acid liberated by scission effects a gradual transformation of the camphene hydrochloride into *iso*bornyl chloride (m. p. 158°, IV). The same process takes place rapidly when camphene hydrochloride is heated to 130 or 140° in a sealed tube, or when it is digested with methylalcoholic or ethereal hydrochloric acid at ordinary temperature. For this reason the so-far applied method of preparing camphene hydrochloride—saturation of the concentrated ethereal or alcoholic solution of camphene with hydrochloric acid and recrystallisation of the resulting product from a methyl-alcohol solution of hydrochloric acid—could only lead to an *iso*bornyl chloride containing camphene hydrochloride. We further understand why the literature records



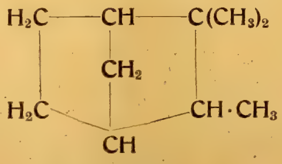
Tricyclene. Camphene hydrochloride. Camphene.



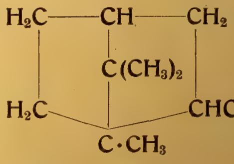
(I) Tricyclene.



(II) Compound with bivalent carbon atom, not capable of existence.



(III) *Iso*camphane.



(IV) *Iso*bornylchloride.

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[1]) The constitution of this dibromide is not quite certain yet. — [2]) Cf. *Report* **1916, 119.**

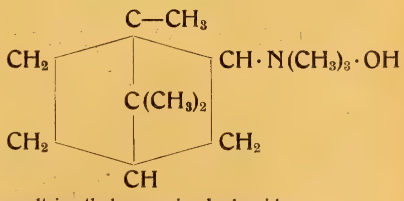
so many different melting-point values (118 to 135°)[1], for the so-called camphene hydrochloride.

The identification and quantitative estimation of the camphene hydrochloride may be based upon its behaviour, in the cold, towards seminormal alcoholic lye. The chloride can easily be titrated with this lye. By means of a simple mode of titration the authors investigated the transformation of the camphene hydrochloride into *iso*borneol, and they observed that this transformation is never completed and that a state of equilibrium is established between *iso*bornyl chloride and camphene hydrochloride, and possibly also pinene hydrochloride. As a matter of fact *iso*bornyl chloride changes when heated for a short time partly into camphene hydrochloride. These two bodies behave, therefore, like tautomeric compounds. The transition of the camphor series into the camphene series may be traced back to the same cause. These transformations are probably true intramolecular displacements of the atoms, that is to say, there is a direct change of place between the alkyl radicle and the halogen atom.

As regards the fact that the camphene obtained from active or inactive borneol, and the *iso*borneol from camphene are always inactive, the authors suggest the following supposition. In addition to the main reaction *iso*borneol $\leftrightarrows$ camphene hydrate $\rightleftarrows$ camphene, there is a subsidiary reversible reaction, *i. e.*, the formation of tricyclene from camphene hydrate, and the racemisation of the camphene and of the *iso*borneol takes place indirectly, *via* tricyclene. This hypothesis would also account for the easy racemisation of the camphene by acids, as well as for the occurrence in camphene of small quantities (about 0.4 per cent.) of tricyclene (obtained from *iso*borneol). The transformations taking place in the absence of acids must, on the other hand, lead to optically-active preparations, since in this case the reversible secondary reaction of the tricyclene-formation would be absent. Thus Lafont[2] obtained from camphene optically-active *iso*borneol, and the experiments of Ipatiev[3] justify the expectation of the preparation of an optically-active camphene from *iso*borneol.

Bornylene.—Since it had not been possible in cases of direct scission of bornyl derivatives altogether to avoid the Wagner[4] transformation and to obtain bornylene free of camphene and other by-products, L. Ruzicka[5] has worked out a process by means of which he obtains, with the help of bornyl trimethylammonium hydroxide, pure bornylene (m. p. 111 to 112°; uncorr., in non-recrystallised crude products).

The bornyl trimethylammoniumiodide (m. p. 245°, uncorr.) prepared after Leuckart[6] and Forster[7], was by treatment with silver oxide converted into the hydroxide and further, by distillation in a high vacuum (one eighth mm.), at least partially into bornylene (m. p. 111 to 112°). By means of methyl iodide an *iso*bornyltrimethylammonium iodide (m. p. 278 to 279°, with decomposition) could be prepared from the by-products of this reaction. The author presumes that we have here to deal with an ordinary borneol-*iso*borneol isomerism, and that the iodide, from which he started, already represented a mixture of stereo-isomerides, corresponding to the bornylamine of Forster[8].



Bornyltrimethylammoniumhydroxide.

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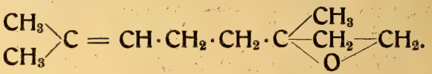
[1] Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 304, record melting points between 142 and 164°. — [2] *Ann. chim.* [6] 15 (1888), 151, 172. — [3] *Berl. Berichte* 45 (1912), 3211. — [4] Cf. *Report* 1919, 115. — [5] *Helvet. chim. acta* 3 (1920), 748. — [6] *Liebig's Annalen* 269 (1892), 347. — [7] *Journ. chem. Soc.* 75 (1899), 945. — [8] *Journ. chem. Soc.* 77 (1900), 1152.

Alcohols.

In his first communication on the *determination of alcohols in the form of allophanates* A. Béhal[1]) had pointed out that linalool occupies a singular position among the terpene alcohols, and that it does not give a crystalline allophanate with cyanic acid as other alcohols do. In order to explain this peculiarity of linalool, A. Béhal now[2]) supposes that the compound is not an alcohol, but an oxide of the following constitution:—



This hypothesis was supported by the observation that, heated with water up to 210°, linalool changes into geraniol. The other properties of linalool so far known would not be contradictory to Béhal's view. An attempt to condense linalool with dimethylamine in the cold was not successful.

The author could further prepare from pure nerol (b. p. 115 to 117° [17 mm.]; d_{15° 0.8832; $\alpha_D \pm 0°$; n_{D15° 1.47593) the allophanate (m. p. 101.5°) which on saponification again gave a nerol with the following constants:—b. p. 115 to 117° [17 mm.]; d_{15° 0.881; $\alpha_D \pm 0°$; n_{D15° 1.47539.

Condensations of n-*butyl alcohol* and n-*butyl aldehyde* have been effected by Ch. Weizmann and St. F. Garrard[3]). The butyl alcohol, which is also formed in the fermentation of glycerin and of mannose caused by moulds, was obtained by the authors as a by-product in the preparation of acetone by fermentation of starch or other carbohydrates with the aid of *Bacillus amylobacter*. By this process, from 8 to 9 per cent. of the starch are converted into acetone, 16 to 17 per cent. into *n*-butyl alcohol, and a small quantity into *iso*propyl alcohol; 25 per cent. of the starch were lost in equal proportions of hydrogen and carbon dioxide. The *n*-butyl aldehyde was prepared, partly by direct oxidation of the butyl alcohol with sodium dichromate and sulphuric acid (yield only 30 per cent. of the theoretical), partly by the catalytic process of Bouveault[4]) with the aid of finely-distributed copper heated to 300°, from butyl alcohol (yield almost theoretical).

n-Butyl aldehyde, which easily undergoes the "aldol" condensation, gave the respective aldol with a yield of 60 to 70 per cent., the latter losing during distillation at ordinary pressure water and forming the α-ethyl-α,β-hexene-aldehyde $CH_3CH_2CH_2CH:C\cdot(C_2H_5)CHO$ (b. p. 172 to 173°, semicarbazone, m. p. 132°).

By reduction with aluminium amalgam the unsaturated aldehyde yielded α-ethylhexyl alcohol $CH_3CH_2CH_2CH_2CH(C_2H_5)CH_2OH$ (b. p. 180 to 185°). Oxidation of the aldehyde with silver oxide and barium hydroxide gave the unsaturated α-ethyl-α,β-hexenic acid $CH_3CH_2CH_2CH:C\cdot(C_2H_5)COOH$ which, by reduction with zinc and sulphuric acid, was transformed into α-ethylhexoic acid $CH_3CH_2CH_2CH_2CH(C_2H_5)COOH$ (b. p. 224°; amide m. p. 101.5°).

The action of metallic sodium, in different quantities and at different temperatures, on *n*-butyl alcohol yielded octyl alcohol, *n*-butyric acid, some octoic acid and traces of esters, ethers and dodecyl alcohol. The quantities obtained of octyl alcohol and of *n*-butyric acid were proportional, within narrow limits, to the amount of sodium present. The temperature influenced merely the reaction velocity. The reaction proceeds in the following two stages:—

$$(1)\quad C_4H_9\cdot OH + C_4H_9\cdot ONa = C_8H_{17}OH + NaOH$$
$$(2)\quad C_4H_9\cdot OH + NaOH = C_4H_7O_2Na + 4H.$$

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[1]) Cf. *Report* 1920, 131. — [2]) *Bull. Soc. chim.* IV. 25 (1919), 452. — [3]) *Journ. chem. Soc.* 117 (1920), 324. — [4]) *Bull. Soc. chim.* IV. 3 (1908), 118.

When sodium hydroxide acts on *n*-butyl alcohol, some 80 per cent. of sodium butyrate are the chief product; further, with a great excess of butyl alcohol, small quantities of *α*-ethylhexyl alcohol and *α*-ethylhexoic acid. Ethyl alcohol, on the other side, yielded under the same considitions only small quantities of acetic acid. Metallic calcium had a similar effect on *n*-butyl alcohol as sodium, but the yield of *α*-ethylhexyl alcohol was small and that of *n*-butyric acid was minimal.

By means of sodium there were obtained, from a mixture of *n*-butyl alcohol and ethyl alcohol, as chief products, *α*-ethylhexyl alcohol and hexoic acid, further *n*-butyric acid and very little *n*-hexyl alcohol, acetic acid and *α*-ethylhexoic acid. Passed over aluminium oxide at 380 to 400°, *α*-ethylhexyl alcohol yielded quickly octylene (b. p. 121°) which, when shaken with 80 per cent. sulphuric acid, was a polymerised into a hydrocarbon $(C_8H_{14})n$ of pleasant odour, probably dioctylene (b. p. 245 to 250°).

Treated with 10 per cent. potassium hydroxide *n*-butyl aldehyde and acetone were condensed into an aldol which on distillation yielded *n*-butylidene acetone $CH_3CH_2CH_2CH:CHCOCH_3$, a colourless liquid turning quickly yellow on exposure to air (b. p. 157°, semicarbazone m. p. 118°). When butylidene acetone was passed over reduced copper oxide at a temperature of 700 to 800°, a small quantity of toluene and a phenolic body, probably cresol, were produced.

When *n*-butyl alcohol and acetone were passed over aluminium oxide at 300 to 350°, several products could be isolated:—methylamyl ketone (b. p. 148 to 150°), a heptadiene C_7H_{12} (b. p. 94 to 96°), further an unsaturated alcohol, probably an isomeride of amyl ketone, and substances which boiled between 70 and 80° (13 mm.) and between 100 and 110° (13 mm.), in addition to traces of *n*-butyl aldehyde and *iso*propyl alcohol. The mixture of *n*-butyl aldehyde and acetone, passed in molecular proportions over aluminium oxide at 300 to 350°, yielded in the first instance butylidene acetone which, on dehydration, gave two hydrocarbons C_7H_{10}, probably of the formulæ $CH_3CH_2CH_2CH:C:C:CH_2$ (?) (b. p. 60 to 70°), and $CH_3CH_2CH_2CH:CH\cdot C\vdots CH$ (b. p. approx. 100°).

Pulegol.—By the reduction of pulegone in alcoholic solution with the calculated amount of metallic sodium Tiemann and Schmidt¹) had obtained a pulegol which was not free of menthol. In order to prepare pure pulegol, which had not yet been isolated, V. Paolini²) resumed the work of Tiemann and reduced pure pulegone (b. p. 221 to 222°; $[\alpha]_D + 22.85°$) by means of sodium in alcoholic solution. He obtained a product which left in the steam distillation a yellow resinous residue (30 per cent.), the part distilled (70 per cent.) being of alcoholic character. The residue seemed to be identical with the bis-pulegone $C_{20}H_{34}O_2$ which Harries and Roeder³) had obtained in the reduction of pulegone by means of aluminium amalgam; the constitution of this body is not quite settled, however. Probably a mixture of optical isomerides was being dealt with.

From the distillate Paolini was able to isolate—by means of the acid phthalic esters, both by the method used⁴) in the pure preparation of the isomeric thujyl alcohols and with the aid of the strychnine compounds—*l*-menthol (m. p. 44°; b. p. 214° [corr.]; $[\alpha]_D - 49.10°$); *d*-menthol (m. p. 88 to 89°; b. p. 214°; $[\alpha]_D - 21.8°$); and *l*-pulegol (m. p. 44 to 47°; $[\alpha]_D - 54.6°$). The intermediate products, prepared and partly identified by elementary analysis, were:—the strychnine salt of the phthalic acid-*l*-monomenthylester (m. p. 157 to 158°; $[\alpha]_D - 44.46°$); the strychnine salt of the

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¹) *Berl. Berichte* **29** (1896), 914. — ²) *Rend. della R. Accademia dei Lincei, Roma* **28** (1919), II. 190. Reprint was kindly sent to us. — ³) *Berl. Berichte* **32** (1899), 3367. — ⁴) Cf. *Report* October **1911**, 142.

phthalic acid-*d*-monomenthylester (m. p. 207 to 208°; $[\alpha]_D - 11.70^\circ$); the phthalic acid-*d*-monomenthylester (m. p. 107 to 108°; $[\alpha]_D - 107.50^\circ$); the phthalic acid-*d*-monomenthylester (m. p. 107 to 108°: $[\alpha]_D + 18.40^\circ$); the phthalic acid-*l*-monopulegylester (m. p. 212°; $[\alpha]_D - 86.80^\circ$). The bromination of *l*-pulegol yielded a product, the bromine percentage of which was slightly diminished by the distillation to less than would correspond to the formula $C_{10}H_{16}OBr_2$. This peculiarity stands in need of an explanation.

Carvomenthol.—Since carvomenthol contains three asymmetric carbon atoms, eight optically-active modifications are possible, as in the case of menthol. V. Paolini[1]) succeeded in decomposing inactive carvomenthol (b. p. 218°) which he had obtained from carvone (b. p. 224 to 225°; d_{20° 0.9596; $[\alpha]_D + 62.4^\circ$) into *l*- and *d*-carvomenthol. The author applied the same method which he had found useful in the investigation of other terpene alcohols[2]). The method is briefly this:—Work without any heating and prepare characteristic crystallisable double salts of the acid phthalate and various bases of organic or inorganic character.

Thus Paolini prepared from the inactive carvomenthol the strychnine salt of *l*-monocarvomenthyl phthalate (m. p. 155 to 156°; $[\alpha]_D - 14.76^\circ$) and from this further the *l*-monocarvomenthyl phthalate (m. p. 125°; $[\alpha]_D - 3.80^\circ$) and *l*-carvomenthol (b. p. 218° [corr.]; d_{15° 0.9082; $[\alpha]_D - 1.82^\circ$; n_{D15° 1.461). He further isolated the silver salt of the *d*-monocarvomenthyl phthalate (m. p. 109°; $[\alpha]_D + 4.62^\circ$) and *d*-carvomenthol (b. p. 218° [corr.]; d_{15° 0.9082; $[\alpha]_D + 1.82^\circ$; n_{D15° 1.461).

Terpin.—According to O. Fernandez and N. Luengo[3]) only one of the hydroxyl groups of this glycol is acetylated when terpin is treated with acetic anhydride and anhydrous sodium acetate. When, however, a solution of terpin in oil of turpentine is treated in the same way, the acetylation is complete.

As regards *piperitol*, see page 23 of this *Report.*

Aldehydes.

The process for the *preparation* of *aldehydes* and *ketones* from primary and secondary alcohols, which is described by Ch. Moureu and G. Mignonac[4]) and which is very suitable in the case of alcohols of low molecular weight, gives less good yields with compounds of higher molecular weights. The authors have now[5]) succeeded in getting over this difficulty by treating the alcohols with oxygen, as before at 230 to 300° and in the presence of a catalyst, but at diminished pressure (20 to 40 mm.).

By this modified method the authors have obtained benzaldehyde and cinnamic aldehyde (yield 80 to 90 per cent.), methylhexyl ketone and dodecyl aldehyde (yield 80 per cent.) further from geraniol, without any noticeable decomposition, citral.

In a paper on the Doebner reaction R. Ciusa and G. Zerbini[6]) state that they obtained by the action of an *aldehyde* upon *pyroracemic acid* and *β-naphthylamine,* in addition to the main product, a β-naphthocinchonic acid, the corresponding tetrahydro compound and yet a second by-product. Thus they prepared from anisaldehyde:—α-anisyl-β-naphthocinchonic acid $C_{21}H_{15}O_3N$ (m. p. 283°), the tetrahydro derivative $C_{21}H_{19}O_3N$ (m. p. 234°) and *p*-methoxybenzyl-β-naphthylamine $C_{10}H_7NH \cdot CH_2 \cdot C_6H_4O \cdot CH_3$

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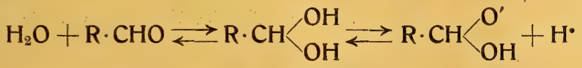
[1]) *Rend. della R. Accademia dei Lincei, Roma* 28 (1919), II. 82. Reprint kindly sent to us. — [2]) Cf. *Report* October **1911**, 142; October **1915**, 79, 80; **1917**, 149. — [3]) *Journ. Soc. chim. Ind.* **39** (1920), A. 704. — [4]) Cf. *Report* **1920**, 132. — [5]) *Compt. rend.* **171** (1920), 652. — [6]) *Gazz. chim. ital.* **50** (1920), II. 317.

(m. p. 98°); from piperonal: — piperonyl-β-naphthocinchonic acid $C_{21}H_{13}O_4N$ (m. p. 292°), the tetrahydro derivative $C_{21}H_{17}O_4N$ (m. p. 233°) and methylenedioxy-benzyl-β-naphthylamine $C_{10}H_7NH\cdot CH_2C_6H_3O_2CH_2$ (m. p. 119°).

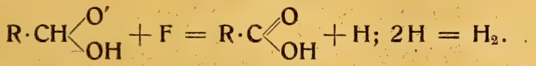
The electrochemical and chemical oxidation of *formaldehyde, aceticaldehyde* and *benzaldehyde* in alkaline solution has extensively been investigated by E. Müller[1]). In the electrolysis of these aldehydes in alkaline solution by means of specially-prepared copper and silver electrodes, a generation of hydrogen was realised simultaneously and in equal quantities, at both the electrodes.

The same process ensued, when purely-chemical oxidation reagents, like cupric oxide, cuprous oxide and metallic copper, acted on the alkaline aldehyde solutions.

The author presumes on the basis of these experiments that aldehydes quite generally undergo, by the oxidation in alkaline solution under certain conditions, a reaction which may be expressed by the following equations: —



$$H_2O + R\cdot CHO \rightleftarrows R\cdot CH{<}^{OH}_{OH} \rightleftarrows R\cdot CH{<}^{O'}_{OH} + H^{\cdot}$$



$$R\cdot CH{<}^{O'}_{OH} + F = R\cdot C{<}^{O}_{OH} + H;\ 2H = H_2.$$

R here indicates an alkyl or hydrogen, and F the charge which has been brought up by electrochemical or chemical oxidation. Müller designates this reaction, which liberates hydrogen, as a dehydroxidation. In the purely-chemical action of copper oxide and silver oxide hydrogen is liberated, not at once, but after an incubation period. This period can be shortened or eliminated by adding from the start metallic copper, silver, or also platinum or palladium. The slowly-proceeding reaction has first to supply the metal so as to make the dehydroxidation appreciable.

In the electrolysis with copper anodes the latter takes place only at low anode potentials. In the measure as this potential is raised, the anode is polarised: — the quantity of catalysing copper is diminished, and the oxidation predominates more and more.

Ketones.

In a previous memoir I. Guareschi[2]) had proved that in the presence of ammonia and of amines most ketones combine with the ester of the cyano-acetic acid to a *cyclo*dicyanoglutarimide (I) which could, by liberating a saturated hydrocarbon, be converted into *cyclo*dicyanoglutaconimide (II) or, by the elimination of two atoms of hydrogen, into trimethylenepyrrole derivatives (III).

In a further paper[3]) the author discussed which ketones do not, or do only incompletely, react with the ester of the cyano-acetic acid, and in how far there is any correlation between this reaction and the reaction with sodium bisulphite. By the aid of the cyano-acetic reaction it can be ascertained, it would appear, whether a compound has the character of a ketone or of an aldehyde.

In the first part of the present paper it is shown that methylbenzylketone and and benzylacetone react both with sodium bisulphite and with the cyano-aceticester, that ethylphenylethylketone and benzyl-*iso*butyl ketone do not combine with bisulphite and combine only to a small extent with cyano-acetic ester, and that propylbenzylketone

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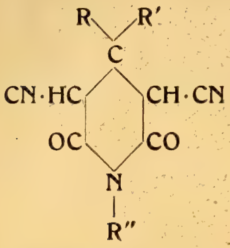
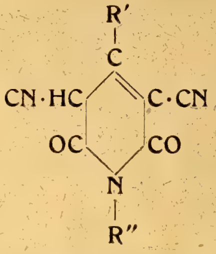
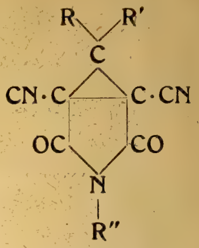
[1]) *Liebig's Annalen* **420** (1920), 241. — [2]) *Memorie della R. Accad. delle Scienze di Torino* [2] **50** (1900), 235. — [3]) *Gazz. chim. ital.* **48** (1918), II. 83; from *Chem. Zentralbl.* **1919**, I. 724.

and *iso*propylbenzylketone yield reaction products with this ester. The methyldicyanoglutarimide is a compound which, sublimed, crystallises in needles or prisms of m. p. 255 to 257°. As regards the descriptions of the other compounds prepared we have to refer our readers to the original.


(I) Derivative of *cyclo*dicyanoglutarimide.

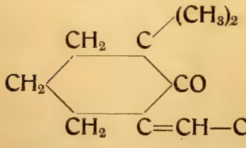

(II) Derivative of *cyclo*dicyanoglutaconimide.


(III) Trimethylenepyrrole derivative.

In paper on 1:3-dimethyl*cyclo*hexanone-2 K. v. Auwers and F. Krollpfeiffer[1]), a few years ago, drew attention to the point, that certain preparations like the numerous hydro-aromatic polyalkylketones, which Haller[2]) had prepared and described, had not been pure compounds but mixtures. The authors showed then that in the methylation of the 1-methyl*cyclo*hexanone-2, according to the method of Haller, far more of the asymmetrical dimethyl derivative is formed than the statements of Haller would lead one to suppose. Further, not only the asymmetrical dimethyl*cyclo*hexanone, as Haller states, but also the symmetrical derivative will react with benzaldehyde. It followed that the method of purification of Haller could not lead to the desired result.

Without making any detailed reference to the justified criticism by v. Auwers, A. Haller and R. Cornubert[3]) have resumed their enquiry into the constitution of *dimethyl*cyclo-*hexanone* as prepared by the methylation of sodium-α-methyl*cyclo*hexanone. They produced in this way a very pure dimethyl*cyclo*hexanone (b. p. 170.5 to 171° [corr.]; $d^{20.5°}_{4°}$ 0.9137; $n_{D20.5°}$ 1.4880; mol. refr. 36.92 [calc. 37.00]), the constants of which were in accord with those which v. Auwers and Lange[4]), Meerwein and Unkel[5]), and v. Auwers and Krollpfeiffer[6]) had obtained, both in asymmetrical and symmetrical preparations. From the ketone, α'-benzylidene-α:α-dimethyl*cyclo*hexanone (I, m. p. 82 to 82.5°) was obtained by condensation with benzaldehyde in the presence of sodium ethylate, with a yield of 26 per cent. This body being identical with the benzylidene compund which K. v. Auwers and Krollpfeiffer had prepared from pure 1:1-dimethyl*cyclo*hexanone, it would follow that Haller's dimethyl*cyclo*hexanone must likewise be asymmetrical.

They further attempted to effect the condensation of dimethyl*cyclo*hexanone with benzaldehyde in another way, by means of gaseous hydrochloric acid, which v. Auwers had likewise proposed. In this reaction they obtained, in addition to the benzylidene derivate described, a lemon yellow, oily benzylidene dimethyl*cyclo*hexanone (b. p. 197 to 198° [corr. 28 mm.]), and further two other, probably anomalous condensation products of 1 molecule of dimethyl*cyclo*hexanone and 2 molecules of benzaldehyde ($C_{22}H_{24}O_2$, m. p. 117 to 118° and 188 to 190°).


(I) α'-benzylidene-α:α-dimethyl*cyclo*hexanone.

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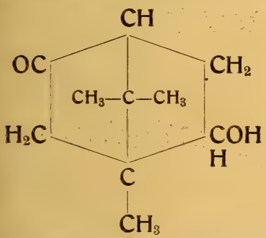
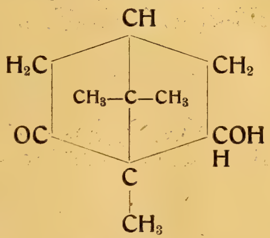
[1]) *Berl. Berichte* **48** (1915), 1226. — [2]) Cf. *Report* April **1915**, 97. — [3]) *Compt. rend.* **170** (1920), 700. — [4]) *Liebig's Annalen* **401** (1914), 303. — [5]) *Ibidem* **376** (1910), 152. — [6]) *loc. cit.*

By the treatment of *paeonol* with nitric acid in glacial acetic acid A. Sonn¹) prepared nitropaeonol and by reduction of this compound the corresponding aminopaeonol (m. p. 115°, uncorr.). Sonn further prepared, by condensation of nitropaeonol with anisaldehyde, 3-nitro-4-methoxy-6-hydroxyphenyl-4-methoxy-styryl ketone (m. p. 182° uncorr.). The likewise prepared aminostyryl ketone melted at 203° (uncorr.).

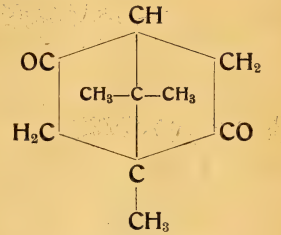
Hydroxycamphor (Ketoborneol).—By means of chromic acid in glacial acetic acid H. Schrötter had in 1881 prepared, from a mixture of bornyl acetate and *iso*bornyl acetate, a body $C_{12}H_{18}O_3$ which, saponified with caustic potash, gave a hydroxycamphor $C_{10}H_{16}O_2$. J. Bredt and A. Goeb²) nowshow that the so-far unexplained constitution of this body (m. p. 238 to 246°; phenylurethane, m. p. 119°) probably corresponds to that of a *p*-ketoborneol (I). The hydroxyl and the carbonyl groups were proved to be present by the acetylation of this body (acetate of the hydroxycamphor, m. p. 76 to 77°) and by the formation of its semicarbazone (m. p. 222 to 224°). In the oxidation of the hydroxycamphor by means of chromic acid the authors obtained a diketone (*p*-diketo-camphane (III), m. p. 206.5 to 207°) which characterised it as a secondary keto-alcohol (ketol). From the corresponding disemicarbazone they obtained, by reduction after Kishner-Wolff (with sodium ethylate in a sealed tube at 200°)³), camphane (m. p. 156°) and, similarly from the hydroxycamphor semicarbazone, pure borneol (m. p. 203 to 204°).



(I) *p*-Ketoborneol (Hydroxycamphor).



(II) *m*-Ketoborneol.



(III) *p*-Diketocamphane.

It was thereby established that the camphor-skeleton was preserved, both in the diketone and in the hydroxycamphor. Since the Schmiedeberg and Manasse hydroxycamphors⁴) differed essentially from the Schrötter hydroxycamphor mentioned, the position of the carbonyl relative to the hydroxyl group could only conform to one of the two formulæ (I) and (II). The ketone obtained was, however, optically-active and should, therefore, be asymmetrically-constituted and have the two CO-groups in *p*-position (III). The corresponding hydroxycamphor should, therefore, also be credited with the constitution of a *p*-ketoborneol (I).

By the reduction of the hydroxycamphor by means of sodium and boiling alcohol the corresponding glycol (*p*-dihydroxycamphane, m. p. 233 to 234°) and from this the diacetate (b. p. 151.5° [15 mm.]) was obtained.

Since the melting points of Schrötter's hydroxycamphor varied in the different preparations between 238 and 246° and were never quite sharp, always indicating a slight decomposition of the product, he had evidently been dealing with a mixture of two stereo-isomerides, an exo- and an endo-form, corresponding to borneol and to *iso*borneol. The exo-form (m. p. 237.5 to 238°) was easily isolated by treatment with zinc chloride according to the method applied by Bertram and Walbaum⁵) in the dehydration of *iso*borneol.

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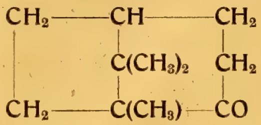
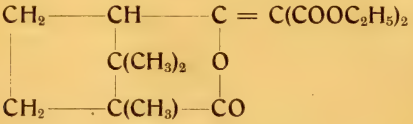
¹) *Berl. Berichte* **54** (1921), 358. — ²) *Journ. f. prakt. Chem. N. F.* **101** (1920), 273. — ³) *Liebig's Annalen* **394** (1912), 86. — ⁴) *Berl. Berichte* **30** (1897), 659; **35** (1902), 3811. — ⁵) *Journ. f. prakt. Chem. N. F.* **49** (1894), 8.

The attempt to replace the hydroxyl group in hydroxycamphor by means of thionyl chloride by chlorine yielded, instead of the expected hydroxycamphor chloride, the sulphite ester of hydroxycamphor $C_{20}H_{30}O_5S$ (m. p. 187°). The oxidation of the acetyl hydroxycamphor with nitric acid did not yield the intended acetylated, dibasic hydroxy acid, but the already-known *p*-diketocamphane. Saponification had taken place in spite of the acid character of the solution, and there had been a secondary oxidation of the CH·OH-group into the carbonyl group.

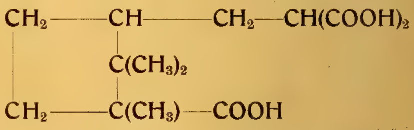
In order to prepare *homocamphor* (I), which differs from camphor only by another CH_2-group in the ketone ring, A. Lapworth and F. A. Royle[1]) prepared first, by the Winzer process[2]), camphorylmalonic ester (II) from camphoric acid anhydride and reduced the ester then by one of the following methods. They applied either sodium amalgam and carbonic acid or they had recourse, with still better results, to electrolysis under definite conditions. By hydrolysis of the reduction product they obtained the hydrocamphorylmalonic acid (III). From this body they obtained by distillation Winzer's hydrocamphorylacetic acid (IV) (carbon dioxide being split off) which was finally converted into homocamphor, either by heating the lead salt of the acid in a current of carbon dioxide, or by the prolonged action of acetic acid anhydride upon the acid and distillation in a vacuum.



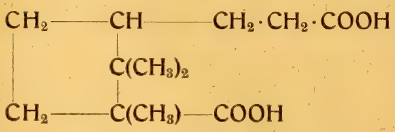
(I) Homocamphor.



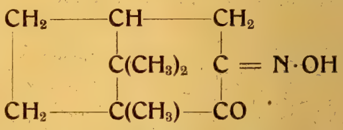
(II) Camphorylmalonic ester.



(III) Hydrocamphorylmalonic acid.



(IV) Hydrocamphorylacetic acid.



(V) *Iso*nitrosohomocamphor.

Homocamphor (m. p. 189 to 190°; $[\alpha]_D - 112.9°$ [4 per cent. solution of benzene]) is a white, indistinctly crystalline mass which resembles camphor in smell and in its behaviour towards the ordinary reagents. The body formed a semicarbazone (m. p. 250 to 252°) which crystallised in colourless needles, and an oxime (m. p. 167 to 168°) which crystallised in long needles. When a small quantity of this oxime was heated with concentrated sulphuric acid the smell of campholenonitrile (raspberries) became noticeable. From the *iso*nitrosohomocamphor (V; m. p. 167 to 168°), pale-yellow crystals were obtained in very small quantities by the action of formaldehyde and hydrochloric acid, representing probably homocamphorquinone.

The correctness of their constitutional formula for homocamphor was proved by the authors by converting *iso*nitrosohomocamphor with acetyl chloride and subsequent

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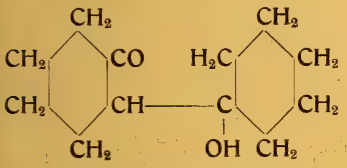
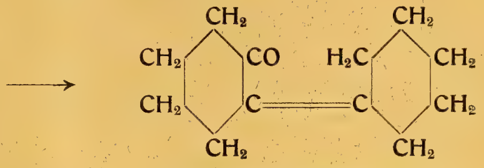
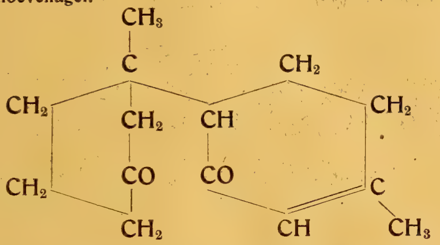
[1]) *Journ. chem. Soc.* **117** (1920), 743. — [2]) *Liebig's Annalen* **257** (1890), 298.

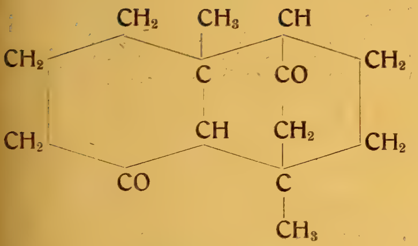
hydrolysis by means of alkali into homocamphoric acid. This homocamphoric acid had the m. p. 233° and the acid value 106 (calculated 107).

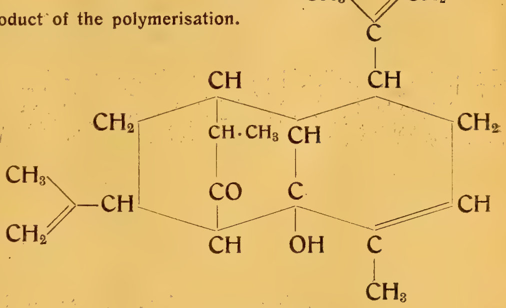
The constitution of the *polymerisation products* of *1:2*-cyclo*hexenones* has not yet been established with certainty. The opinion of Knoevenagel[1]) that these bodies probably have the constitution of a β-keto-alcohol of the type (I) is very improbable according to Ruzicka, because a compound of this kind cannot be isolated in the case of the saturated ketones, but yields at once, under loss of water, a dimolecular unsaturated ketone (II). Ruzicka[2]) showed that dimerides of *cyclo*hexenones form, with acetic acid anhydride, quantitatively monoacetates, so that the second oxygen atom would be bound in the hydroxyl group, and further that bis-1:3-methyl*cyclo*hexenone has a double bond in its molecule. These facts, as well as the observation, common in the case of α:β-unsaturated ketones, that additive combinations with reactive methylene are not taking place in the carbonyl group, but at the double bond of carbon atoms, led Ruzicka to the conclusion that the first reaction-product to be considered in the polymerisation of *cyclo*hexenones is a diketone of the formula (III). The further course of the polymerisation is indicated by the additive compound between acetic ester and *cyclo*hexenone, as explained by Rabe and his collaborators[3]). Analogous to these processes studied by Rabe there are, in the just-mentioned primary additive products (III), two possibilities


(I) Unstable polymerisation product of 1:2-*cyclo*hexenone, Knoevenagel.


(II) Dimolecular unsaturated ketone.


(III) First reaction product of the polymerisation.


(IV) Saturated diketone.


(V) Biscarvon.

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[1]) *Berl. Berichte* 32 (1899), 423. — [2]) *Helvet. chim. acta* 3 (1920), 781. — [3]) *Report* October 1904, 126.

for further condensations, especially of the dimethyl*cyclo*hexenone: either — and that will be the most common case — an unsaturated keto-alcohol is formed, or a saturated diketone (IV) will result. The formation of this diketone need only be considered with respect to a secondary reaction (once observed) in which the bis-1:3-methyl*cyclo*hexenone (b. p. 200 to 205°, [12 mm.]) yields two different disemicarbazones, *viz.*, of the diketone (m. p. 246°) and of the keto-alcohol (m. p. 215°).

Since the ketones studied by Ruzicka comprise all the types of the 1:2-*cyclo*hexenones with substitutes in the 1, 2 and 3 positions relative to the carbonyl, the polymerisation which he describes may be assumed to represent a general phenomenon in this group. The polymerisation was effected by means of sodamide and proceeded all the more smoothly, the more amide was used in the reaction. We further mention the following compounds prepared by Ruzicka: — *Dihydro-bis-1:3-methyl*cyclo*hexenone* (b. p. about 200°, 13 mm.; acetate, m. p. 220°); *bis*-iso*phorone,* b. p. 203 to 205° (17 mm.), or 140° ($^1/_5$ mm.), semicarbazone, m. p. 215°, acetate, b. p. about 200° (12 mm.); *bis-carvone* (V), b. p. 225° (12 mm.), semicarbazone, m. p. 194 to 195°, with evolution of gas, acetate b. p. about 225° (11 mm.).

As regards *piperitone,* see page 23 of this *Report.*

Phenols and Phenol Ethers.

Some phenols including *carvacrol* and *thymol* can, as is well known, be extracted from their alkaline solutions by means of ether[1]). Störmer and Kippe[2]) proved that the sodium-compounds of carvacrol can so be extracted by ether from a 30 to 40 per cent. caustic-soda solution, but that thymol under the same condition passes almost entirely into the ether as pure phenol (without sodium). D. C. L. Sherk[3]) has conducted further experiments in this direction and has found that both carvacrol and thymol dissolved in 5 per cent. caustic soda, when shaken with ether, pass into this solvent without any combination with sodium taking place. Of thymol up to 99.89 per cent. are extracted from the alkaline solution by means of ether; in the case of heptane, carbon tetrachloride, carbon disulphide and benzene the extraction was only partial, amounting to 30 to 68 per cent. How carvacrol behaves under the same conditions is not stated in the paper.

By the method, recommended by F. Weehuizen for the preparation of *phenylurethanes*[4]) (application of a petroleum-fraction boiling between 170 and 200° as solvent) D. C. L. Sherk[5]), starting with about 2 to 5 g. of material, obtained 71 per cent. of thymolphenylurethane (m. p. 106.5 to 107°); 86 per cent. of carvacrolphenylurethane (m. p. 138°; the m. p. of 140° which E. Gildemeister[6]) determined was not reached by Sherk); 84 per cent. of thymohydroquinone-di-phenylurethane (m. p. 232 to 233°); 43 per cent. of thymol-α-naphthylurethane (m. p. 156 to 157°); 35.9 per cent. of carvacrol-α-naphthylurethane (m. p. 119°); and a small yield of thymohydroquinone-mono-α-naphthylurethane (m. p. 147 to 148°). The preparation of m. p. 287 to 288°, which C. Neuberg and E. Hirschberg[7]) had obtained by heating α-naphthyl*iso*cyanate and carvacrol, was, as Sherk shows, not a carvacrol-α-naphthylurethane, but probably a decomposition-product of α-naphthyl*iso*cyanate. Sherk further prepared by the method of Schotten-Baumann (with sodium hydroxide and benzoylchloride) dibenzoylthymohydroquinone (m. p. 141 to 142°).

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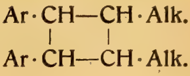
[1]) *Berl. Berichte* **32** (1899), 1517. — [2]) *Ibid.* **36** (1903), 3992. — [3]) *Americ. Journ. Pharm.* **93** (1921), 8. — [4]) *Report* **1919**, 130. — [5]) *Americ. Journ. Pharm.* **93** (1921), 115. — [6]) *Arch. der Pharm.* **233** (1895), 188. Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. I, p. 474. — [7]) *Report* April **1911**, 172.

Some years ago E. Puxeddu1) had prepared, by the action of ferric chloride upon ethereal anethole, a new *polymeric anethole* $(C_{10}H_{12}O)_{10}$, a white powder melting above 300°. Distilled in a vacuum (260°) this body yielded a further polymeric anethole $(C_{10}H_{12}O)_2$ (prismatic needles, m. p. 132°, little soluble in ether)2). The author assumes that the polymers of anethole posses the annexed tetramethylene structure. There would thus be eleven stereo-isomers.



$$\begin{array}{c} Ar \cdot CH - CH \cdot Alk. \\ \quad | \qquad\quad | \\ Ar \cdot CH - CH \cdot Alk. \end{array}$$

Puxeddu further studied the homologues of anethole, the *p*-butenyl and the *p*-*iso*-pentenylanisole which had already been prepared by Ch. Moureu and A. Chauvet3). From the *p*-butenylanisole (b. p. 245 to 248°), which had been prepared by heating (for eight hours) anisaldehyde, butyric acid anhydride and sodium butyrate to 275°, the author obtained, in the polymerisation with ferric chloride in ether, an oily product.

p-*Iso*pentenylanisole (b. p. 248 to 252°, n_D 1.54), soluble in ether and alcohol, which was similarly prepared from anisaldehyde, *iso*valeric acid anhydride and sodium *iso*-valerate, yielded a dibromide (m. p. 93 to 95°). The polymerisation of the latter gave a gummy product.

Acids, Esters, and Lactones.

Rather and Reid4) have found that, owing to their high melting points, *acids* are sometimes better identified with the aid of their phenacylesters than by their *p*-nitrobenzylesters. Still more suitable for this identification, particularly of monobasic aliphatic acids (dibasic acids are well characterised as phenacylesters), are the *p*-halogenphenacylbromides because they mostly form, with the acids, esters of high melting points5).

The three halogenphenacylbromides were easily prepared according to a method described by Collet6) from monohalogenbenzene and bromoacetylchloride (reaction of Friedel and Crafts). The esters themselves Rather and Reid obtained by the method which they had several times already described in detail4), by heating the monobasic acids (with the exception of the acetic, propionic, glycolic and lactic acids) for one hour, dibasic acids for two hours, and tribasic acids for 3 hours, on the water bath. A few acids, like asparaginic, maleic, racemic, tartaric and meconic acids, could not be identified by this method, as their esters decomposed before melting. Some other acids, gallic, linolic, oleic, oxalic, monochloroacetic and trichloroacetic, proved equally unsuitable for this determination. Of the many esters which these authors prepared we mention here:—(1) the *p*-chlorophenacylester of acetic acid (m. p. 67.2°), of benzoic acid (m. p. 118.6°), of thiocyanic acid (m. p. 135.2°), of tricarballylic acid (m. p. 125.6°); (2) the *p*-bromophenacylester of acetic acid (m. p. 85.0°), of anisic acid (m. p. 152.0°), of benzoic acid (m. p. 119.0°), of cinnamic acid (m. p. 145.6°), of phenylacetic acid (m. p. 89.0°), of salicylic acid (m. p. 140.0°), of palmitic acid (m. p. 81.5°), of thiocyanic acid (m. p. 146.5°), of *o*-toluylic acid (m. p. 56.9°), of valeric acid (m. p. 63.6°); (3) the *p*-iodophenacylester of acetic acid (m. p. 114.0°), of benzoic acid (m. p. 126.5°), of *iso*-valeric acid (m. p. 78.8°), of palmitic acid (m. p. 90.0°), of valeric acid (m. p. 78.6°).

On the whole the bromo-derivative is preferable to the two other *p*-halogenphenacylbromides as reagent. From the *p*-halogenphenacylesters the corresponding alcohols could easily be obtained by hydrolysis with water containing barium carbonate. In this way the authors prepared the *p*-chloro-, *p*-bromo- and *p*-iodophenacyl alcohols (m. p. 122.4°, 136.6° and 152.0°).

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1) *Report* **1917**, 152. — 2) *Gazz. chim. ital.* **50** (1920), I. 149. — 3) *Bull. Soc. chim.* III. **17** (1897), 411. — 4) *Journ. Americ. chem. Soc.* **41** (1919), 75. — 5) *Ibidem* **42** (1920), 1043. — 6) *Compt. rend.* **125** (1897), 717.

A. Grün[1]) has published a paper on the constitution of the *acids of colophony resins.* The author discusses the relations between the structural formulæ of pinene-hydrocarbons and abietic acids. Similarly as the latter might be considered to have been formed from pinene-hydrocarbons, constitutional formulæ might also be deduced for certain resin-acids from the structures of the camphene and the fenchene, which are present in small quantities in oils of turpentine.

D. H. Brauns[2]) has prepared the *menthylesters* of the *higher aliphatic acids* by heating the respective acid chloride with menthol. The latter was best obtained by the action of thionyl chloride upon the aliphatic acid. In this way Brauns prepared the following esters: — menthyllaurate $C_{22}H_{42}O_2$; liquid at ordinary temperature; $d^{20^\circ}_{4^\circ}$ 0.8915; $[\alpha]_D$ — 46.07°; mol. refr.$_{20^\circ}$ 155.9; menthylmyristate $C_{24}H_{46}O_2$; m. p. 21 to 22° (Hilditch[3]) m. p. 32°); $d^{20^\circ}_{4^\circ}$ 0.882; $[\alpha]_D$ — 42.33°; mol. refr.$_{20^\circ}$ 155.1; menthylpalmitate $C_{26}H_{50}O_2$; m. p. 32; $d^{20^\circ}_{4^\circ}$ 0.8848; $[\alpha]_D$ — 30.10°; mol. refr.$_{20^\circ}$ 154.2; menthylstearate $C_{28}H_{54}O_2$; m. p. 38 to 39°; $d^{45^\circ}_{4^\circ}$ 0.8665; $[\alpha]_D$ — 36.60°; mol. refr.$_{45^\circ}$ 154.6; menthylarachate $C_{30}H_{58}O_2$; m. p. 55°; $d^{55^\circ}_{4^\circ}$ 0.8566; $[\alpha]_D$ — 30.63°; mol. refr.$_{55^\circ}$ 138.0.

A paper by M. Gomberg and C. C. Buchler[4]) concerns the preparation of various *benzylesters* and of other benzyl derivatives by means of benzyl chloride. Pure preparations in good yields (up to 85 per cent.) were realised when the benzyl chloride and the aqueous solution of the salts of organic acids were heated for longer periods while being stirred. In this way were prepared:—benzylbenzoate (b. p. 310 to 315°; the boiling point of another preparation obtained from the dry salt was 323°; the boiling point of Claisen[5]) was 323 to 324° [corr.]); benzylacetate (b. p. 205 to 210°); benzylpropionate (b. p. 220 to 230°); benzylbutyrate (b. p. 235 to 242°); benzylphenylacetate (b. p. 204 to 210° [20.5 mm.]); benzylcinnamate (b. p. 240 to 244° [25 mm.]); benzylsalicylate (b. p. 211 to 214° [22.5 mm.]); dibenzylsuccinate (m. p. 47 to 48°). The formic, oxalic and phthalic acids did not yield any benzylesters.

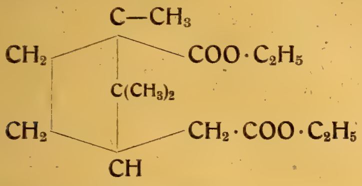
With sodium phenolates (phenol and α- and β-naphthol), treated in the same way, benzylchloride gave mixtures of benzylethers and of benzylphenols; the constants of these preparations are not stated. Benzylcyanide (with 50 to 60 per cent. yield) was likewise obtained by heating (for 1 to 4 hours) benzylchloride with sodium cyanide in aqueous solutions. Finally the authors established that benzylchloride was more quickly converted into benzylalcohol by caustic soda than by sodium carbonate.

In the synthesis of camphor- and fenchone-ketones, which consist only of 5-membered and 6-membered rings, dry distillation of the calcium and lead salts of *dicarboxylic acids* (homocamphoric acid and analogues) had so far been applied in most cases. The necessarily-high temperatures might in bodies of the classes of tri- and tetraceanic systems lead to scission of the ring. L. Ruzicka and W. Kuhn[6]), therefore, tried the sodium condensation of such esters of dicarboxylic acids which proceeds at lower temperature, in the first instance with the ester of the homocamphoric acid (I). This compound (m. p. 170 to 172° [12 mm.]) the authors prepared by heating ethyl camphorcarboxylate (II) with sodium ethylate in an autoclave for 24 hours up to 200° and treating the product with concentrated hydrochloric acid. The sodium condensation of the ester of homocamphoric acid (boiling for four hours 4 g. of ester with 0.45 g. of

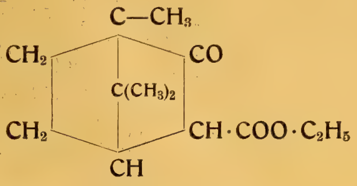
---

[1]) *Zeitschr. d. Deutschen Öl- u. Fettind.* **41** (1921), 40. — [2]) *Journ. Americ. chem. Soc.* **42** (1920), 1478. — [3]) *Journ. chem. Soc.* **101** (1912), 192. — [4]) *Journ. Americ. chem. Soc.* **42** (1920), 2059. — [5]) *Berl. Berichte* **20** (1887), 647. — [6]) *Helvet. chim. acta* **3** (1920), 752.

sodium in 6 cc. of xylene on the oil bath) yielded the camphorcarboxylate easily; by boiling with concentrated hydrochloric acid the latter was converted into camphor with a yield of 68 per cent.

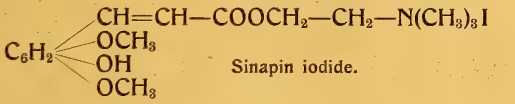


(I) Diethyl homocamphorate.



(II) Ethyl camphocarboxylate.

E. Späth1) has realised the synthesis of *sinapin,* which is contained in black mustard and which Gadamer2) considers as an ester of the sinapic acid (3:5-dimethoxy-4-hydroxy-cinnamic acid) and of choline, in the following way:—From trimethylgallic acid he prepared the carbethoxysyringic acid and from this, by means of hydrogen and palladinised barium sulphate by the method of Rosenmund3) carbethoxysyringinaldehyde $C_6H_2CHO^{[1]}(OCH_3)_2^{[3,5]}OCOOC_2H_5^{[4]}$ (m. p. 100 to 101°) which, saponified with caustic soda in a vacuum, yielded quantitatively syringinaldehyde $C_6H_2CHO^{[1]}(OCH_3)_2^{[3,5]}OH^{[4]}$ (m. p. 112 to 113°). Carbethoxysyringinaldehyde gave, heated with malonic acids and glacial acetic acid, a good yield of benzylidene malonic acid, from which he obtained carbethoxysinapic acid and sinapic acid $C_6H_2 \cdot CH{=}CH \cdot COOH^{[1]}(OCH_3)_2^{[3,5]}OH^{[4]}$ (m. p. 190 to 191°); this last acid was identical with the acid prepared from natural sinapin. By decomposition of acetylsinapin hydrochloride with hydroxy-ethyldimethylamine Späth prepared the β-dimethylamino-ethylester of acetylsinapic acid, the acetyl group of which was removed by shaking the ethereal solution with 5 per cent. caustic soda in an ice-cooler. From the hydroxy-ethyldimethylamine ester of the sinapic acid a quaternary iodide (m. p. 185 to 187°) was prepared by means of methyl iodide; this product, as well as the rhodanide (m. p. 180 to 181°) and the acid sulphate (m. p. 190 to 191°) prepared from it, agreed in all their properties with the corresponding salts of the natural sinapin.



$$C_6H_2\left\langle\begin{array}{l} CH{=}CH{-}COOCH_2{-}CH_2{-}N(CH_3)_3I \\ OCH_3 \\ OH \\ OCH_3 \end{array}\right.$$

Sinapin iodide.

P. Karrer, A. Glattfelder and Fr. Widmer4) report on the synthetic preparation of *bergaptene* and *xanthotoxin.* Both these compounds occur in the oil of *Fagara xanthoxyloides,* Lam., and bergaptene alone in bergamot oil; they are coumarone-coumarine derivatives and have according to Pomeranz, Thoms, and Thoms and Baetcke the formulæ I and II5).

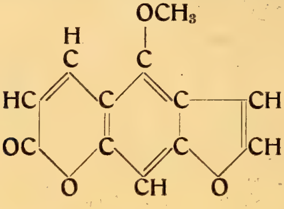
Wishing first to prepare the simplest possible coumarone-coumarine derivatives, they attempted to convert the 2-methyl-5-hydroxycoumarone-4-aldehyde (m. p. 181°) in analagy to the coumarine-synthesis of Perkin, by means of acetic acid anhydride and sodium acetate into the corresponding coumarine. Instead of the intended body they obtained a well-crystallised compound which, boiled with water, soon formed the 2-methyl-5-hydroxycoumarone-4-acrylic acid $C_{12}H_8O_3$ (m. p. 114°). It is strange that this

---

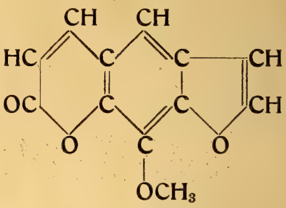
1) *Monatsh. f. Chem.* 41 (1920), 271. — 2) *Arch. der Pharm.* 235 (1897), 95. — 3) *Berl. Berichte* 51 (1918), 585. — 4) *Helvet. chim. acta* 3 (1920), 541. — 5) Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. II, p. 632 and vol. III, p. 64.

acid showed not the slightest inclination to pass into the corresponding coumarine. Why this ring formation was not possible has not yet been ascertained. The authors presume, however, that there is a steric hindrance to ring-formation of the atoms in this reaction.

In order to build up coumarone-coumarine derivatives without the methyl group the authors prepared the 5-hydroxycoumarone $C_8H_6O_2$, so far unknown (m. p. 56°), from 7-acetoxycoumarine by means of the bromine compound and, further, the 5-hydroxycoumarone-4-aldehyde $C_9H_6O_3$ (partly decomposed at 260°). The Perkin reaction did not convert this aldehyde either into the corresponding coumarine.



(I) Bergaptene.



(II) Xanthotoxin.

All attempts to prepare the lactone *α-campholide* (I) having so far given little satisfactory results, H. Rupe and A. Jäggi[1]) have worked out a method which is based upon the reduction of camphoric anhydride according to Sabatier and Senderens and which yielded 98 per cent. of the theoretically-possible α-campholide. Attention had to be paid in the reduction to the suppression of disturbing secondary reactions which took place when the temperature of the electric furnace was not kept within 220 to 240°.

The lactone crystallised from ligroin in stout needles and had the m. p. 210 to 211°.

The vapours escaping especially at too high temperatures of the furnace were conducted from the reduction tube through a wash bottle, cooled in ice, condensed and separated into the following fractions by means of repeated fractionations over metallic sodium:—(1) 108 to 115°; (2) 115 to 120°; (3) 120 to 125°; (4) 125 to 132°; (5) 132 to 230°. The first four fractions were mobile colourless liquids, the last fraction was yellow and rather viscous; whilst fractions 3 and 4 contained oxygen, the first two fractions consisted of probably unsaturated hydrocarbons of the formula C_9H_{16}.

By the method of v. Baeyer and Villiger[2]) the authors prepared from the α-campholide (by means of a solution of hydrogen bromide in glacial acetic acid) bromocampholic acid (II), melting at 177° with decomposition); by modifying the method to a slight extent (passing the hydrogen bromide into the solution of α-campholide in glacial acetic acid) they were able to raise the yield from 60 to 80 per cent. of the theoretical.

Starting from bromocampholic acid they prepared:—the chloride (m. p. 57.5°), the amide (m. p. 207°), the anilide (m. p. 142°), the phenylhydrazide (m. p. 150 to 151°), the methylester (b. p. 139° [15 mm.]), the ethylester (b. p. 142 to 143°, m. p. 9 to 10°), the phenylester (m. p. 46 to 47°). Attempts to prepare an additive compound of the bromocampholate with magnesium failed. On the other hand the methyl bromocampholate reacted with benzylmagnesium chloride and yielded a body which probably had the constitution of a 1:2:2-trimethyl-3-phenylethyl-*cyclo*pentane-1-benzylketone (III, m. p. 119°).

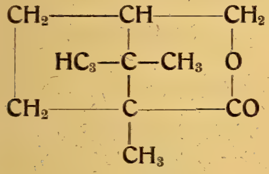
From the behaviour of the bromocampholate towards reagents which would split off halogen hydrides, it could be demonstrated that the *cyclo*pentane ring was not

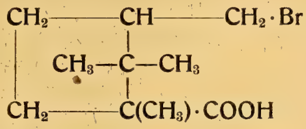
---

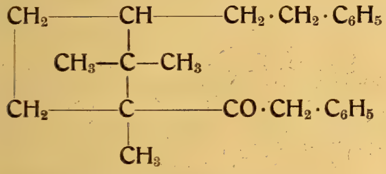
[1]) *Helvet. chim. acta* 3 (1920), 654. — [2]) *Berl. Berichte* 32 (1899), 3631.

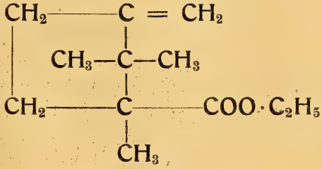
broken up in this case. The compound formed is in fact a semicyclic methylene compound, such as the 1 : 2 : 2-trimethyl-3-methylene-*cyclo*pentane-1-carboxethylate (IV, b. p. 93° [12 mm.]) which was obtained by boiling bromocampholate with an alcoholic solution of sodium ethylate. By reduction of α-campholide with sodium, 1:2:2-trimethyl*cyclo*pentane-dimethanol-1:3 (V, m. p. 130°) was prepared.

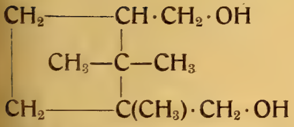
Finally the authors mention a process by means of which they prepared α-camphidone (VI, m. p. 233°) and camphidine (VII, m. p. 182°) from the campholide, respectively the glycol (V) by heating with ammoniacal zinc chloride. These bodies had already been obtained by Tafel and Eckstein[1]) from the imide of camphoric acid.

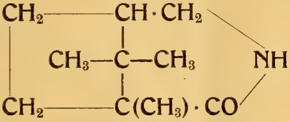

(I) α-Campholide.

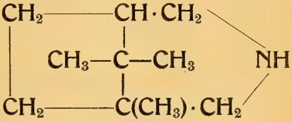

(II) Bromocampholic acid.


(III) 1:2:2-Trimethyl-3-phenylethyl-*cyclo*pentane-1-benzylketone.


(IV) 1:2:2-Trimethyl-3-methylene-*cyclo*pentane-1-carboxethylate.


(V) 1:2:2-Trimethyl-*cyclo*pentane-dimethanol-1:3.


(VI) α-Camphidone.


(VII) Camphidine.

Glucosides.

Since the ordinary chemical determinations of dextrose fail in the presence of some other sugars, Em. Bourquelet and M. Bridel[2]) have worked out a new, biochemical process which is specific only for dextrose. The method is based upon the property of emulsin to form glucosides from dextrose and alcohol, and it allows of determining this kind of sugar qualitatively and quantitatively in the plants. Thus two parts of dextrose, dissolved in 100 parts of methylalcohol (70 per cent.), formed in the presence of emulsin about 82 per cent. of methylglucoside. This reaction, which is also reversible, does, however, not proceed further. From the change in the angle of rotation of the solution the quantity of glucoside formed and, further, the desired percentage of dextrose are calculated. By means of this method the authors ascertained that the reducing sugar of juniper berries contains 19.5 per cent. of dextrose, and that the glucoside which Bourquelot and Bridel[3]) found in *Loroglossum hircinum,* Rich. consisted partially also of dextrose.

---

[1]) *Berl. Berichte* 34 (1901), 3274. — [2]) *Compt. rend.* 170 (1920), 631. — [3]) Cf. *Report* April 1915, 79.

The glucosides which are contained in the root of the primrose (*Primula officinalis,* Jacq.), *primverin* and *primulaverin*[1]), are hydrolysed by a ferment called primverase into the *p*-methylether of *β*-resorcylic acid or into the same body and into *m*-methoxysalicylic methylester (on the one hand) and into a biose (on the other). This sugar, which A. Goris and Ch. Vischniac[2]) styled primverose, has further been investigated by the same authors. Primverose is soluble in water, in 80 per cent. alcohol and in methylalcohol, melts in the "bloc Maquenne" at 209 to 210°, has initially the specific optical rotation $[\alpha]_D + 22.70°$, and after 24 hours $[\alpha]_D - 3.43°$, reduces Fehling's solution and forms an osazone (m. p. in bloc Maquenne 224 to 226°). The biose is composed of one molecule each of dextrose and xylose.

Nitrogenous Bodies.

In a paper on *cyclo*hexylamine A. Skita and H. Rolfes[3]) describe among other methods the following for the preparation of *cyclo*hexyl mustard oil:—

1. N:N'-di*cyclo*hexylthiocarbamide (I), m. p. 180 to 181°, obtained from *cyclo*hexamine and carbon disulphide, was distilled with glacial phosphoric acid. The distillation product, *cyclo*hexyl-*iso*thiocyanate $C_6H_{11}N:C:S$ (II), a liquid having a stinging smell of mustard oil, boiled at 219° (746 mm).

$$CS\left\langle\begin{matrix}NH\cdot C_6H_{11}\\ NH\cdot C_6H_{11}\end{matrix}\right. \longrightarrow C_6H_{11}N:C:S + C_6H_{11}NH_2$$

(I) N:N'-Di*cyclo*hexylthiocarbamide. (II) *Cyclo*hexyl-*iso*thiocyanate. *Cyclo*hexylamine.

2. The same body was obtained with a better yield by the Hofmann mustard-oil synthesis, by the action of mercuric chloride upon ammonium di*cyclo*hexyl-dithiocarbamate (III), the first reaction product of carbon disulphide and *cyclo*hexylamine.

$$CS\left\langle\begin{matrix}NH\cdot C_6H_{11}\\ S\cdot NH_3\cdot C_6H_{11}\end{matrix}\right. \longrightarrow C_6H_{11}N:C:S + H_2S + C_6H_{11}\cdot NH_2$$

(III) Di*cyclo*hexyldithiocarbamate of ammonium.

The *cyclo*hexyl-*iso*thiocyanate, the fist representative of the hydroaromatic mustard oils is, like the aliphatic and aromatic mustard oils, highly reactive and forms with alcohols and phenols easily thiourethanes and, with ammonia and amines, thiocarbamides.

Referring to this work of Skita and Rolfes, J. von Braun[4]) points out that primary amines containing a non-aromatically bound NH_2-group are most easily transformed into the corresponding mustard oil by means of the thiuramdisulphide method. Braun[5]) and also W. Schneider[6]) proved years ago that this method is particularly suitable for the preparation of fatty-aromatic, hydroaromatic and complex aliphatic mustard oils. The *cyclo*hexyl mustard oil described by Skita and Rolfes could also be obtained from hexahydroaniline in a few minutes with almost theoretical yield.

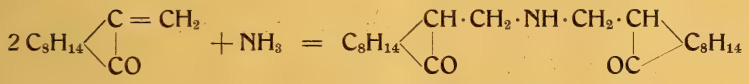
In continuation of two previous researches, in which Rupe reported on the condensation of hydroxymethylene-camphor with various bases concerning stereo-isomerides of aminomethylenecamphor, H. Rupe and W. Kussmaul[7]) attempted to prepare the reduced

---

[1]) Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. III, p. 391. — [2]) *Bull. Roure-Bertrand Fils,* April 1920, 7. — [3]) *Berl. Berichte* 53 (1920), 1242. — [4]) *Berl. Berichte* 53 (1920), 1588. — [5]) Cf. *Report* October 1912, 164. — [6]) Cf. *Report* April 1915, 108. — [7]) *Helvet. chim. acta* 3 (1920), 515.

aminomethylenecamphor, the methylcamphoramine (I). All the attempts of the authors to obtain this body failed, however, both by the reaction of camphylbromomethane with ammonia, and by the reduction of the aminomethylenecamphor. But several other, new compounds were obtained. In the reaction of camphylbromomethane upon ammonia, a secondary base, *dicamphomethylamine,* was formed, the origin of which is explained as follows:— From camphyl bromomethane, ammonia first splits off hydrogen bromide, methylenecamphor being formed; 1 molecule of ammonia then unites with 2 molecules of methylenecamphor.

Camphylbromomethane. Methylenecamphor.



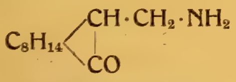
Dicamphomethylamine.

The dicamphomethylamine was further prepared by the direct union of ammonia and methylenecamphor and by the action of ammonia on camphyl-carbinol under pressure. The amine $(C_{11}H_{17}O)_2NH$, an amorphous, white mass of m. p. 124°, formed salts, sparingly-soluble in water, (oxalate, hydrochloride and hydrobromide), a nitroso-amine $C_{22}H_{34}O_3N_2$ (m. p. 106°) and a benzoyl derivative $C_{29}H_{39}O_3N$ (m. p. 132°). The constitution of the amine was determined by preparing it also, by means of reduction with aluminium amalgam in neutral solution, from the already-known methylene-camphorimide.

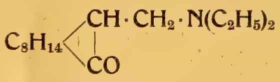
Although the preparation of the primary basis (I) looked-for was not successful, the authors were able to prepare a derivative, the *diethyl-campho-methylamine* (II, b. p. 137° [8.5 mm.]) from methylene camphor and diethylamine.

The reduction of aminomethylenecamphor with aluminium amalgam yielded a secondary basis (III), m. p. 145 to 147°, very similar and isomeric to dicamphor-methylamine, the constitution of which has not definitely been established so far.

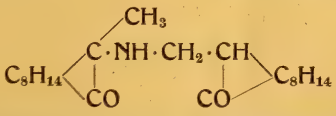
Finally a few quaternary ammonium compounds were prepared, such as methylene-camphor-trimethyl-ammonium chloride, m. p. 162°. This research is not yet completed.



(I) Methylcamphoramine.



(II) Diethyl-campho-methylamine.



(III) Secondary base, isomeric with dicamphomethylamine.

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Distillation of Palmarosa Oil in British India.

(After a water-colour painting in the possession of the Perfumery Department of the German Museum in Munich. Gift of the firm of Schimmel & Co.)

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ANNUAL REPORT

ON ESSENTIAL OILS
SYNTHETIC PERFUMES
&c.

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Contents.

Page
Commercial Notes and Scientific Information on Essential Oils . . . 5
Pharmacopœias . . . 85
Chemical Preparations and Drugs . . . 90
Notes on Scientific Research Work in the Domain of Terpenes and Essential Oils.
- General . . . 103
- Bibliography . . . 108
- Analytical . . . 110
- Physical . . . 115
- Botanical . . . 118
  - Phyto-physiological . . . 121
- Pharmaco-physiological . . . 122
- Chemical . . . 130
  - Hydrocarbons . . . 130
  - Alcohols . . . 138
  - Aldehydes . . . 143
  - Ketones . . . 146
  - Phenols and Phenol Ethers . . . 150
  - Acids, Esters, and Lactones . . . 152
  - Glucosides . . . 154
  - Nitrogenous Bodies . . . 155

List of abbreviations.

d = specific gravity.
d_{20° = specific gravity at 20° (in references from our laboratories uniformly compared with water at 15°).
$d\frac{20^\circ}{4^\circ}$ = specific gravity at 20°, compared with water at 4°.
α_{D20° = optical rotation at 20°, in a 100 mm. tube.
$[\alpha]_D$ = specific rotation.
n_{D20° = index of refraction at 20°.
sol. p. = solidifying point.
m. p. = melting point.
b. p. = boiling point.
n = normal.
acet. = acetylation.
acid v. = acid value; ester v. = ester value; sap. v. = saponification value.
g. = gram; cc. = cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.
The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

Commercial Notes and Scientific Information on Essential Oils.

Oil of Abies Pindrow. — Cones and young shoots of the Indian silver fir, *Abies Pindrow* (Royle) Spach[1]), yielded on steam distillation an oil, of which we received a sample some time ago. It was colourless, of agreeable balmy odour and showed the following constants: — $d_{15°}$ 0.8647, α_D — 10° 59′, $n_{D20°}$ 1.47328, acid v. 0.3, ester v. 6.5 = 2.3 per cent. ester (bornyl acetate), soluble with slight turbidity in 3 volumes and more of 90 per cent. alcohol; soluble in 1 vol. and more of 95 per cent. alcohol.

The tree occurs in the lower Himalaya regions, at a height of between 2400 and 3000 metres.

Oil of Aburachan. — By distillation of the leaves and twigs of *Lindera præcox*. Bl., a lauracea growing in Japan, Y. Shinosaki[2]) obtained about 0.3 per cent. of a light brown coloured oil which had a somewhat strongly camphoraceous odeur and the following characters: — $d_{15°}$ 0.9094 to 0.9178; α — 3° 57′ to — 5° 1′; $n_{D20°}$ 1.4850 to 1.4866; acid value, 0.69 to 0.92; sap. value, 45.76 to 48.69; sap. val. after acetylation, 90.48 to 98.62. The following substances were isolated[3]): — 2 per cent. of α-pinene, 14 per cent. of camphene, 8 per cent. of cineole, 10 per cent. of an aliphatic terpene (b. p. 40 to 41° at 2 mm., $d_{15°}$ 0.8251, $n_{D20°}$ 1.4840), borneol present in the oil partly free and partly as ester, geraniol (23 per cent. with borneol), 8 per cent. of caryophyllene, 21 per cent. of *d*-cadinene, 5 per cent. of a sesquiterpene alcohol $C_{15}H_{26}O$, and a tertiary alcohol (b. p. 140 to 142° at 4 mm.; $d_{15°}$ 0.9740; α — 5°, $n_{D20°}$ 1.5072). From the alkaline liquor after saponification of the original oil there were isolated: — acetic acid, a decylenic acid $C_{10}H_{18}O_2$ (b. p. 106 to 107° at 1.5 mm., $d_{15°}$ 0.9339, $n_{D20°}$ 1.4552, acid value 328 to 334.9, iodine value 142.24, probably identical with citronellic acid) and a saturated weak acid of higher series and having a high boiling point.

Ajowan Oil. — Y. Murayama found in this oil a new terpene, moslene (cf. p. 51 of this *Report*).

Almond Oil, bitter. — A bitter almond oil "genuine, free from chlorine", sent us for inspection, proved an "excellent" acquisition for the buyer, as it was a crude, strongly chlorinated benzaldehyde of a reddish-brown colour (due to iron), containing about 30 per cent. of nitrobenzene.

The defects of the product were revealed at once by its constants, as it was far too heavy ($d_{15°}$ 1.1237), had too high a refraction ($n_{D20°}$ 1.54876) and did not dissolve in 50 per cent. alcohol; besides, it gave a strong chlorine reaction. It resulted on closer investigation that these irregularities were due to nitrobenzene, present in the proportion

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[1]) According to Brandis, this is only a variety of *Abies Webbiana*, Lindley. Comp. A. Engler and K. Prantl, *Die natürlichen Pflanzenfamilien* vol. II, 1, page 60. — [2]) *Journ. chem. Ind. Japan* 24 (1921), 444. According to *Journ. Soc. chem. Ind.* 40 (1921), A. 674. — [3]) Details are missing in the abstract.

indicated above. After having isolated it, it could be identified by its odour and its other properties:— d_{15° 1.2032, n_{D20° 1.55104, solidification point $+3.6^\circ$.

Nitrobenzene being highly poisonous, as we have repeatedly pointed out in our *Reports*[1], its use as an adulterant is inexcusable. We can only take it that the seller was too silly to understand the bearing of his action, otherwise he ought to have realized what ill effects the addition of nitrobenzene to a product often used in the household may have.

As E. Pinoff[2] says, the presence of nitrobenzene in bitter almond oil can easily be proved in the following way:—10 cc. of a 40 per cent. formaldehyde solution and 20 cc. of concentrated ammonia are filled in a cylinder holding 100 cc. and which can be closed with a stopper of india-rubber. After having shaken the mixture carefully for some time, it must be allowed to stand for five minutes. Then it is shaken vigorously with 10 cc. of the bitter almond oil and again allowed to stand. The pure bitter almond forms an emulsion with the formaldehyde-ammonia, whereas the nitrobenzene deposits as a clear liquid. The nitrobenzene is then reduced with zinc and hydrochloric acid to aniline, which can be identified by one of the well-known reactions.

We are of opinion that the usual method, according to which the benzaldehyde is bound to bisulphite, is simpler and more convenient (cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. I, p. 585).

Oil of Amomis jamaicensis.—The oil of *Amomis jamaicensis* (wild pimento), the constants of which we quoted in our *Report* of **1920**, p. 6 after a communication in the *Bulletin of the Imperial Institute*, London, has been further investigated by O. D. Roberts[3]. After removing the free acids (0.2 per cent. acetic and caproic acids), an aldehyde (0.1 per cent.) and a phenol (0.1 per cent., *not* eugenol) the oil was hydrolysed with boiling alcoholic potassium hydroxide and the oil separating after addition of water and extracting with ether was submitted to fractional distillation at 14 mm. pressure, which gave the following fractions:— 1. B. p. 75 to 80° (175 to 190° at ordinary pressure), 32 per cent. of the original oil; 2. b. p. 80 to 95° (190 to 205°, ord. pr.), 42 per cent.; 3. b. p. 95 to 110° (205 to 220°, ord. pr.), 4 per cent.; 4. b. p. 110 to 125° (220 to 235° ord. pr.), 6 per cent.; residue 16 per cent. of the original oil. Fraction 1 contained 47 per cent. cineole = 15 per cent. of the original oil (resorcinol method and iodole addition compound), α-phellandrene (nitrite, m. p. 112 to 113°), and dipentene (tetrabromide, m. p. 124°). The principal part of fraction 2 had the constants:— b. p. 197 to 198°, $d^{15^\circ}_{15^\circ}$ 0.8693, $\alpha_D - 3^\circ 39'$, n_{D20° 1.4655 and was identical with *l*-linalool (oxidation to citral; α-citryl-β-naphthocinchoninic acid, m. p. 200°). In fraction 4 geraniol was proved to be present (diphenylurethane, m. p. 80 to 81°). The residue boiling above 235° was heated on the water bath under reduced pressure for some weeks with sodium. There was thus obtained by distillation under 15 mm. pressure a colourless oil, with a slight balsamic odour, b. p. 245 to 290° (uncorr.), $d^{15^\circ}_{15^\circ}$ 0.9320, which was still slowly attacked by sodium.

The author summarizes his investigation as follows:—The oil of *Amomis jamaicensis* contains about 17 per cent. of terpenes (α-phellandrene and dipentene), 15 per cent. of cineole, 38.3 per cent. of alcohols (chiefly *l*-linalool with some geraniol), 1.5 per cent. of ester (linalyl acetate), each 0.1 per cent. of phenols and aldehydes, both undetermined, 0.2 per cent. of acetic and caproic acids, and 27.8 per cent. residue probably containing sesquiterpenes.

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[1] Cf. for instance *Report* **1918**, 5. — [2] *Pharm. Zentralh.* **62** (1921), 610. — [3] *Journ. Soc. chem. Ind.* **40** (1921), T. 95.

Oil of Andropogon Iwarancusa. — J. L. Simonsen[1] investigated the oil of *Andropogon Iwarancusa,* Jones, a graminea occurring in the Himalayas and the outer hill zone from Kashmir to Assam and ascending to 8000 ft. and above, also in the plains from North West Himalaya to Bombay Presidency. The pale yellow oil, which had been obtained in a 1 per cent. yield from the grass, possessed a marked smell of peppermint and had the following constants: — $d_{30^\circ}^{30^\circ}$ 0.9203, $[\alpha]_{D30^\circ}$ + 51.68°, n_{D30° 1.481, acid v. 0.7, sap. v. 12.0, sap. v. after acet. 47.4, percentage of ketone, by absorption with neutral sodium sulphite solution, 77 per cent. On distilling and refractionating the oil under diminished pressure (200 mm.), the following fractions were obtained: — 1) 115 to 130° (14.6 per cent.), 2) 130 to 174 (1.6 per cent.), 3) 174 to 185° (70 per cent.), 4) 185 to 205° (12 per cent.). The first fraction consisted essentially of a hydrocarbon, b. p. 101° (100 mm.), 163 to 164° (698 mm.), $d_{30^\circ}^{30^\circ}$ 0.8565, $[\alpha]_{D30^\circ}$ + 54.82°, n_{D30° 1.474, smelling pleasantly reminiscent of cymene. When dissolved in acetic anhydride and treated with a drop of sulphuric acid, a transient purple coloration appeared, which rapidly passed into a deep brown. When the hydrocarbon was treated with hydrogen chloride in ethereal solution, an oil resulted which was probably a monohydrochloride; with hydrogen bromide in acetic acid solution a viscous oil was obtained, which was evidently a dihydrobromide $C_{10}H_{18}Br_2$. The hydrogen iodide derivative was very unstable, and decomposed even when kept at 0°. Fraction 2) consisted apparently mainly of a mixture of *d*-Δ^1-*p*-menthenone-3 and the hydrocarbon. Fraction 3) ($d_{30^\circ}^{30^\circ}$ 0.9321, $[\alpha]_{D30^\circ}$ + 36.76°, n_{D30° 1.481) consisted, by 98 per cent., of *d*-Δ^1-*p*-menthenone and was purified by solution in sodium sulphite solution and reprecipitation (and racemisation, comp. Read and Smith, p. 34 of this *Report*) by alkali, when it showed the following constants: — b. p. 180 to 181° (200 mm.), 230 to 231° (697 mm.), $d_{30^\circ}^{30^\circ}$ 0.9307, $[\alpha]_{D30^\circ}$ + 7.92°, n_{D30° 1.481. Fraction 4) still contained a considerable quantity of the ketone. The identity of the racemic ketone with *dl*-Δ^1-*p*-menthenone-3 = piperitone (comp. p. 149 of this *Report*) is proved, according to Simonsen, by the formation of the benzylidene derivative (m. p. 61°) and the hydroxylamino-oxime (m. p. 170 to 171°), furthermore by oxidation of the ketone, by ferric chloride, to thymol and by the reduction to menthol. Besides, the author prepared: — the α-semicarbazone (m. p. 225 to 227°), the β-semicarbazone (m. p. 174 to 176°), an optically active β-semicarbazone (m. p. 193 to 194°), the oxime (m. p. 117 to 118°), and proved thus the identity of his ketone with the Δ^1-menthenone-3 obtained by Wallach and others[2]. The discrepancies observed in the constants as compared with the values found by former authors (α-semicarbazone, m. p. 224 to 226°, β-semicarbazone, m. p. 171 to 172°, oxime, m. p. 107 to 109°) are explained by Simonsen by assuming that the compounds obtained formerly had not been quite pure and free from isomerides.

On oxidising the ketone with potassium permanganate solution, at 0°, *l*,γ-acetyl-α-*iso*propylbutyric acid was obtained; b. p. 195 to 200° (48 mm.).

Thus the oil of *Andropogon Iwarancusa* consists up to 80 per cent. of *d*-Δ^1-menthenone-3 and of a hydrocarbon of unknown constitution.

Angelica Oil. — Last autumn, it is true, the Thuringian plantations supplied abundant quantites of raw material, but the prices remained high, as there was a vivid demand, owing to the completely exhausted stocks of oil. Although we had secured considerable lots, our production was scarcely large enough to come up to the requirements from all quarters, so that we were almost sold out at the beginning of the present year. The prospects are not very favourable, as there are only few

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[1] *Journ. chem. Soc.* **119** (1921), 1644. — [2] Comp. *Reports* October **1910**, 99; **1916**, 18.

fresh plantations in Thuringia which, besides, will yield material for distillation only in 1923. The shortage of oil will therefore continue.

From fresh angelica roots, Roure-Bertrand Fils[1]) obtained by water-and-steam distillation 0.4 per cent. of a golden-yellow oil with the following qualities: — $d_{17.5^\circ}$ 0.8887, d_{15° 0.8907 (corr.), α_{18° $+6^\circ 42'$, acid v. 7.20, ester v. 45.07, sap. v. 52.27; soluble in 2 and more vols. of 90 per cent. alcohol. The odour of the oil was inferior to that obtained from dried roots. The low optical rotation and the high acid and ester values differed from the normal figures. — The oil extracted from aqueous distillate by means of light petroleum showed an odour less intense than that of the principal oil, it was dark red and had the constants: — acid v. 20.53, sap. v. 134.40; soluble in 90 per cent. alcohol with slight opalescence, entirely soluble in 95 per cent. alcohol.

Apple Oil. — Basing on their investigations on the composition of the odorous principle of ripe apples[2]) F. B. Power and V. K. Chesnut[3]) publish particulars of a U. S. Pat. (No. 1366541) for synthetic apple oil. This oil is composed of the *iso*amyl esters of formic, acetic, caproic and caprylic acids, together with acetaldehyde, or of these components without the *iso*amyl caproate. According to the abstract available, the mixture, which may be employed either in the concentrated state or in alcoholic solution, consists of: — *iso*amyl formiate 10 pts., *iso*amyl acetate 10 pts., *iso*amyl n-caproate 5 pts., *iso*amyl caprylate 1 pt., acetaldehyde 2 pts.

As to the paper published by Kodama (comp. p. 154 of this *Report*) and bearing the title: "On the odour of apples; ethereal oils obtained from leucic acid", F. B. Power and V. K. Chesnut[4]) remark that, according to their investigations, the esters prepared by Kodama do not occur in apples[5]). Hence, the title given by Kodama to his communication is not only misleading but entirely unwarranted.

Atlas Cedar Tar. — In the well-wooded region of Azrou, south-east of Meknes, the natives prepare through incomplete combustion of the roots of *Cedrus atlantica,* Manetti, a tar which was recently investigated by R. Massy[6]). The author states that a long pit, lined with clay and situated on an incline, serves for the purpose. The lowest part of it is connected through a narrow pipe with a hole, into which the distillation products flow. After having filled the pit with the pieces of wood from the roots, the largest at the bottom, and covered with branches of the tree and sand, the wood is lit from the side opposite the escape-pipe, left open for the purpose. The slower the combustion, the better the yield. After about twelve hours, the distillate collected in the hole is taken out and filled into a hanging skin bag, in which the tar separates from the water, this then being removed. The distillation is completed after another 24 hours, when the new distillate is treated in the same way. 241 kilos of cedar wood thus yielded 17.78 kilos (7.4 per cent.) of crude tar, corresponding to 4 per cent. of filtered tar. The final product had the following properties: — d_{20° 0.981 to 0.985; on being distilled under ordinary pressure between 150 and 300°, 71 per cent. of a dextrorotatory body passed over. The products carried over by steam are dextrorotatory. Less than 5 c.c. of N/soda lye suffice to neutralize the acid contained in

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[1]) *Bull. Roure-Bertrand Fils,* October 1921, 33. — [2]) Comp. *Bericht* (German) 1921, 7; also the work of Thomae, *Reports* October 1911, 21; April 1913, 28. — [3]) *Perfum. Record* 12 (1921), 123. — [4]) *Journ. Americ. chem. Soc.* 43 (1921), 1741. — [5]) Comp. *Bericht* (German) 1921, 7. — [6]) *Journ. de Pharm. et Chim.* VII. 24 (1921), 264.

100 c. c. of tar, which acid is soluble in cold water. Every 100 c. c. of tar contain 10.3 to 12.8 grams of constituents soluble in 5 per cent. soda lye, precipitable by means of hydrochloric acid and soluble again in ether.

Bay Oil. — According to Robson¹), Curator, Montserrat, the results from the bay tree experiment plot in 1919 were more favourable than ever. Although fifty-two distillations were made of leaves reaped from the plot, it was not possible to deal in the still at the Botanic Station with the total quantity reaped, and therefore 1255 lbs. were sold to a distiller at the close of the year. Several thousand pounds of leaves were left unreaped on account of the unability to deal with them. Once the trees are sufficiently developed actually to cover the ground occupied, less and less cultivation is required. The average yield of oil per 100 lbs. of green leaves in this season on the whole of the distillations was 17.3 ozs., compared with an average of 18.6 in the previous year. The best average results have been obtained between January and July. This, however, may be entirely due to the effect of the usual dry weather at this time of the year, and to the leaves having a reduced water content as the result of evaporation. On the question of the quality of the oil as indicated by the specific gravity and the phenol content, the best results in 1917 were obtained in March, April and May; in 1918, in June and July; and in 1919, in the month of October. A trial was made with old leaves, many of which had been on the trees for at least two years, but the result was disappointing in every respect.

A bay oil from Mexico may be mentioned here just for the sake of its particular origin. It was only slightly inferior in quality to good West Indian oils: — d_{15° 0.9658, $\alpha_D - 1^\circ 50'$, n_{D20° 1.50891, soluble in 0.5 vol. of 80 per cent. alcohol. A further addition of alcohol caused opalescence. The eugenol content, determined with the aid of 3 per cent. soda lye, was 55 per cent.

Birch Tar Oil. — Our repeated endeavours to procure at least small quantities of this product, which originates exclusively from Russia, having failed, it was impossible so far to satisfy the demand for this oil, so indispensible for the manufacture of a good Russian leather perfume. It is quite understandable, however, that the disastrous economic conditions of that country imply that all attention be directed for the time being to more important products, so that the users of the article must wait patiently still longer.

J. Pritzker and R. Jungkunz²) publish an article on the investigation of the oils of birch tar and other wood tars. From the review of previous publications, given by the authors, it results that the indications regarding the definition of birch tar and the parts of the tree used for its manufacture differ considerably. Some say, it is obtained from the bark; others, from bark and twigs, or from the roots, from the wood, etc. The authors failed in their attempts to obtain absolutely pure birch tar. The results of their investigations show great differences, especially with regard to the indices of refraction, which vary between 50.9 and above 100. However, they afford some general information, which may be useful for further tests of birch tar oils.

A product styled „Russian leather fat" (birch tar oil), repeatedly offered in Switzerland, resulted to be a strongly rancid fat, perfumed with some artificial aromatic. Two other birch tar oils were strongly adulterated (more than 50 per cent.) with mineral

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¹) *Chemist and Druggist* 95 (1921), 350. — ²) *Schweiz. Wochenschrift f. Chem. u. Pharm.* 59 (1921), 146, 162.

oils. A pre-war sample of birch tar oil, taken from our research laboratories' collection, showed an extraordinarily high content of unsaponifiable constituents, which was not due to any admixture of mineral oils. A test for resinous matter gave a negative result. Another birch tar oil, surely originating from the neighbourhood of Minsk, had the characteristic Russian leather smell and contained 55 per cent. of resin, as well as 32 per cent. of unsaponifiable matter of pitchlike character.

The author states that Zeiss' butter refractometer answered very well for the determination of refraction, whereas Storch's reaction (anhydrous acetic acid and sulphuric acid) was a useful test for resinous bodies. As tars from conifers consist almost exclusively of resin, but tars from deciduous trees contain very little resin, the indices of refraction of the various tars and of their distillation products afford a means of distinguishing them, especially if the saponification value, the acid value and the amount of unsaponifiable products are likewise taken into consideration.

Oil of Boldo Leaves. — Roure-Bertrand Fils[1]) obtained from the leaves of the boldo tree, *Peumus Boldus*, Mol., *Monimiaceæ,* by distillation with steam, a golden-yellow oil[2]), the odour of which resembled that of cineole and chenopodium oil. It showed the following constants: — $d_{17°}$ 0.9318, $d_{15°}$ 0.9334, $\alpha_{11°}$ $-0° 14'$, acid v. 1.87, ester v. 13.0, cineol content 30 per cent. Besides, the sample investigated contained 10 per cent. of constituents soluble in 3 per cent. soda lye. After having been freed from the alkali and dissolved in alcohol, they gave a greenish yellow colour reaction with ferric chloride. The acetylated oil showed $\alpha_{D15°}$ $+1°$, ester v. 70.93.

On shaking the distillation water of 40 kilograms of leaves with light petroleum, 20 grams of an oil were obtained which was much darker and smelled quite different from the product obtained direct. It had the following properties: — $d_{15°}$ 0.9323, $\alpha \pm 0°$, acid v. 3.73, ester v. 22.40, ester v. after acetylation 142.18. The authors think that the high acetylation value is due to decomposition products of the ascaridole. The acetylated oil smelled distinctly of terpinyl acetate. With the aid of 5 per cent. soda solution, 15 per cent. phenols were separated from the oil, they smelled of carvacrol and coloured green with ferric chloride.

Oil of Boronia pinnata. — The oil obtained by steam distillation from *Boronia pinnata,* Sm., a *Rutacea* occurring in Australia, showed according to Smith[3]) the following properties: — amber-yellow colour, aromatic odour like geranyl acetate and geraniol, $d_{15°}$ 1.0197, $\alpha + 3.8°$, $n_{D20°}$ 1.5125, saponification v. 20.2, id. after acetylation 36,9, content of geranyl acetate 6.4 per cent. The oil contained also free geraniol, geranyl butyrate, trimethyl gallic acid and 70 per cent. elemicin $C_{12}H_{16}O_3$[4]).

Oil of Buchu Leaves. — As per the annual statement of trade and shipping of the Union of South Africa[5]), the exports of buchu leaves were as follows: —

1919	149166 lbs. to the value of	37130 £
1920	139149 „ „ „ „ „	67243 „.

The average annual export for the five years 1910 to 1914 was 204271 lbs., valued at 30394 £, while the average for the five years 1915 to 1919 was 130161 lbs., valued

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[1]) *Bull. Roure-Bertrand Fils,* April 1921, 14. — [2]) Nothing is said about the yield. — [3]) *Proceed. Royal Soc. Victoria N. S.* 1 (1919), 32. According to *Bull. Roure-Bertrand Fils,* April 1921, 113. — [4]) There are no other details. — [5]) *Chemist and Druggist* 94 (1921), 745.

at 23937 £. The world's demand for both the buchu leaves and oil is rapidly increasing, and the future prospects of buchu as a field crop are good, so that increased interest is being taken in the cultivation of the plant.

Cade Oil. — There are two methods1) of preparing cade oil; *viz.*, the *"destillatio per descensum"* for small amounts and the *"combustion en milieu confiné"* for large quantities. As A. Juillet2) says, Planchon described in 1911 a new apparatus, which is more easily worked and is said to give better yields than the old furnaces. Planchon avails himself of the *"destillatio per descensum"*, which he has improved somewhat and carries out on a larger scale. A jug-like container of a capacity of 1 cbm., being 1.70 m. high and having a diameter of 0.5 m. in the centre, is used for the dry distillation of the wood. This furnace, the walls of which are made of bricks and are about 15 cm. thick, stands on an inclined stone plate, has a small opening on top (diameter 20 to 25 cm.?) and another at the bottom, which is superficially closed during the distillation with a flat stone. A strong hemispherical brick-work, which has several apertures at the bottom, surrounds the furnace in such a way that the distance between the two walls (45 cm. at the bottom, decreases gradually higher up, but the opening on top is left free. Through the latter the furnace is filled with pieces of wood of *Juniperus Oxycedrus,* 6 to 25 cm. long. Then the opening is shut by means of a flat stone and earth and a fire is made in the space between the two walls and kept up for twelve hours. After this time, the walls are so hot that the distillation continues for another 6 to 8 hours. The distillation products, flowing out of the lower opening, are collected in a large vessel and treated in the well-known way3).

With this furnace, used in the departments of Gard and Hérault (Sommières), about 4 to 6 kilos of cade oil can be obtained in one distillation from 250 kilos of wood. This yield seems susceptible of an increase.

The author remarks that there would now be again more demand for genuine cade oil, as there was a method of distinguishing between the pure product and faked stuff4). The cheap adulterated products form Norway and Asia Minor have no therapeutic value at all, whereas the genuine article is an excellent remedy against skin diseases, especially for animals.

Mr. B. Ménaché5), of Barcelona, estimates that 80 tons of pure cade oil are produced yearly in Spain, 30 tons of which are consumed locally, and the balance of about 50 tons are available for export. The cade tree, *Juniperus Oxycedrus,* L., grows in abundance only in the hilly and rocky districts, this is to say far away from railways and even carriage-roads. To give an idea of the distance between "civilization" and the cade growing country, Mr. Ménaché mentions that it takes a two hours' carriage journey, followed by a six hours' ride on horseback, to go from the railway station to his nearest stills, fitted up in 1920 according to the French system6), but with iron stills.

Although the best oil is obtained from the roots alone, generally roots and stems are distilled together. Such genuine oils, obtained by Mr. Ménaché in various places, had the following properties: — d_{15° 0.955 to 0.990, completely soluble in ether, soluble with slight opalescence in 20 vols. of 90 per cent. alcohol, colour like burnt sugar.

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1) Comp. *Report* November **1908**, 24. — 2) *Parfum. moderne* **13** (1920), 165. — 3) Comp. *Report* November 1908, 25. — 4) It is to be regretted that the author does not give any details. We would refer to Huerre's investigations, which might perhaps be useful for the test of cade oil (*Report* **1919**, 9). — 5) *Perfum. Record* **12** (1921), 149. — 6) *Berl. Berichte* **47** (1914), 2258.

Years ago, H. Huerre[1] showed that direct distillation of the wood of *Juniperus Oxycedrus* yielded 8.11 per cent. of cade oil, or, if the essential oil had previously been removed, only 5.62 per cent. of distillate. In a new treatise, Huerre[2] examines the relations between the content of essential oil in the wood and the yield of cade oil. The raw material for his experiments was coarsely powdered wood of *Juniperus Oxycedrus,* from which the essential oil had been drawn by steam distillation and the resin extracted by means of ether and acetic ether. This material was subjected to dry distillation, partly with an admixture of 3 to 5 per cent. of the essential oil of *Juniperus Oxycedrus,* partly without. During the distillation, which took four hours, the temperature rose after less than two hours from 98 to 203°, then sank to 180° and remained constant till the end. In the interior of the wood, it reached 402° and remained constant, after two hours, between 380 and 385°. Six different experiments, carried out in this way, had the following results: — 1) In the presence of 5 per cent. essential oil: 9 per cent. oil, lighter than water, 32 per cent. water, 9 per cent. tar, 37.5 per cent. charcoal. 2) Without any addition: 0 per cent. light oil, 36 per cent. water, 2.5 per cent. tar, 37.5 per cent. charcoal.

Huerre concludes from these results that the essential oil of *Juniperus Oxycedrus* passes over completely with the cade oil and serves as a solvent for the heavy tar. The author's other observation that during the distillation cadinene is transformed only to the extent of 20 to 25 per cent. is not new, for F. W. Semmler and W. Jakubowicz[3] have shown already that a large proportion of cadinene remains unaltered at a temperature of 330°.

It had been taken for granted that the brown colouring with copper acetate and light petroleum sufficed to characterize genuine cade oil. According to H. Huerre[4], "cade oil for veterinary use", the origin of which is unknown, gives the identical reaction, the same as the essential oils obtained by dry distillation from other conifers, with the exception of *Pinus maritima* (Poir. or Mill.?). The oils of *Juniperus Virginiana,* L., and *Cedrus Libani*, Barrel., the same as cade oil, yield after treatment with dilute soda lye on distillation under normal pressure 55.5 and 62.5 per cent., respectively, of fractions passing over between 250 and 300°, in addition to a distillation residue of 7.5 and 10 per cent., respectively. The author intends to publish shortly an article on a new reaction of cade oil (by means of the dihydrochloride of cadinene).

A treatise by R. Massy[5] deals with the tars obtained from African conifers as substitutes for cade oil. The author describes the botanical origin of these products (*Thuja, Juniperus* and *Cedrus* species), the methods of production and the principal properties of the tars.

Cajuput Oil. — The export figures for the provinces of Ambon and Celebes, including those of the island of Boeroe, are now available up to 1918. The direct exports, chiefly via Singapore, were: —

	1916	1917	1918
to British India and China	84 000 kilos	77 000 kilos	33 000 kilos
besides, to Java	71 000 „	83 000 „	79 000 „ .

Java re-exports a considerable part of its imports. The Javanese use the oil not only as an embrocation for contusions, excoriations, wounds and head-aches, but also against bugs.

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[1] *Bull. Sciences pharmacol.* 28 (1921), 299. As per *Chem. Zentralbl.* **1921**, IV. 812. — [2] *Bull. des Trav. de la Soc. de Pharm. de Bordeaux,* June **1921**. According to a reprint kindly sent us. — [3] *Berl.-Ber.* **47** (1914), 2077. *Report* April **1915**, 85. — [4] Comp. above. — [5] Comp. *Report* **1919**, 8.

The chief shipping place is Macassar, the official statistics of which port show the considerable fluctuations of the last years.

The shipments were: —

1914	381	cases or baskets	1918	624	cases or baskets
1915	4481	„ „ „	1919	2802	„ „ „
1916	3359	„ „ „	1920	1324	„ „ „
1917	1546	„ „ „	1921	1805	„ „ „ .

The investigation of a cajuput oil, sent us for the purpose, showed once again very clearly that the constants alone are not always a safe criterion for the quality of the oil. Specific gravity, rotatory power and solubility were altogether normal (d_{15° 0.9209, α_D — 0° 36′, soluble in 1 vol. and more of 80 per cent. alcohol) but the odour proved that the product consisted chiefly of a camphor oil fraction containing cineole, which had been adjusted to the constants of cajuput oil. The camphor-like odour was so unmistakable that a special chemical proof was not required.

A great lack of moral sense is required to place such stuff on the market and this case shows again how necessary it is to buy only from reliable firms.

Camphor Oil. — The exports of camphor oil from Japan, after a considerable rise in 1920, decreased very much in 1921. In the years from 1919 to 1921, they were as follows[1]): —

1919	10306	piculs to the value of	333785 yen
1920	23424	„ „ „ „ „	841508 „
1921	8056	„ „ „ „ „	167256 „ .

An extensive article in the *Bulletin of the Imperial Institute*[2]) on the "Present position of the camphor industry" deals with the history and the prospects of camphor production in China, Japan and Formosa. In addition the cultivation of the camphor tree in Italy, Algeria, South Africa, West Usambara, America, the West Indies, Buenos Aires, Burma, the Nilgiris, the Straits Settlements, the Federated Malay States, Queensland, Ceylon, Madagascar, Mauritius and the Canaries is discussed with more or less details. As our readers will already be fairly well acquainted with the subject, we only extract from the article what can serve as a completion of our previous communications.

Formerly, camphor came to Europe almost entirely in the crude state, from China, Formosa, or Japan, the process of refining being a Dutch secret at the close of the seventeenth century and afterwards a Venetian monopoly, but more recently carried out in England, Hamburg, Paris, New York and Philadelphia, as well as in Japan. 1912 it was estimated that 70 per cent. of the world's consumption of camphor[3]) — then 11000000 lbs. — was used for the manufacture of celluloid. Since then, the rapid increase of the cinematograph industry has led to a greatly enlarged demand for it as a material for the manufacture of films and similar products, such as xylonite. The total amount of camphor taken by Europe and the United States in 1914 is said to have been 12000000 lbs.

The Chinese export of camphor in 1891 (before the cession of Formosa) was 17000 piculs (over 2250000 lbs.), and, according to a Chinese authority, the province of Fukien alone had in 1905 more camphor trees than Formosa. Between 1903 and 1907, the province was overrun by Japanese employés and, according to the Chinese

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[1]) *Chemist and Druggist* 96 (1922), 468. — [2]) *Bull. Imp. Inst.* 18 (1920), 524. — [3]) It is supposed that in the ten first years of this century 7 to 10 million lbs. were consumed annually, on an average, in the whole world, as compared with 17 million lbs. in 1916, 12 million lbs. in 1917 and 10 million lbs. in 1913.

authority already quoted, the Japanese saw that it was only by rapidly destroying the industry in Fukien that they could create a monopoly for themselves. The export of camphor from Foochow rose from 264 cwts. in 1902 to 13535 cwts. (1516600 lbs.) in 1906. As all the available trees were cut down and no planting took place, the industry rapidly declined afterwards, as shown by the following table.

Total Chinese Exports of Camphor in Pounds:—

1907 . .	3433937 lbs.	1912 . .	331000 lbs.	1915 . .	181735 lbs.
1908 . .	1742933 „	1913 . .	248700 „	1916 . .	316933 „
1911 . .	448133 „	1914 . .	241333 „	1917 . .	472933 „.

The revival under the stimulus of rising prices which is here shown after 1915 came mainly from the province of Kiangsi, in which there are stated to be camphor forests and some undeveloped territory, especially in the south. In 1919 Kiukiang alone produced 332266 lbs., and the following statistics[1]) show how considerably the Chinese camphor export has revived again since 1919.

Exports of Camphor from China:—

1916	2377 piculs	(316850 lbs.)	181673 tæls
1917	3547 „	(472800 „)	261918 „
1918	5742 „	(765400 „)	428074 „
1919	23093 „	(3078300 „)	1595313 „
1920	29997 „	(3998600 „)	2840043 „.

American buyers are looking to China for an immediate addition to the supply, as in the Shan States of South-West Yunnan there are stated to be an immense number of camphor trees only awaiting transport facilities for their exploitation. The Chinese authority already quoted recommends that an American Syndicate should start operations in South Hunan and South Kiangsi, establishing distilleries on modern lines, cutting in a conservative manner, and encouraging planting by demonstration plantations, lectures, pamphlets, and the free distribution of seed and seedlings, and should afterwards extend their action into Kweichow, Kwangtung and Kwangsi.

In Japan, the export, which had been over 6577000 lbs. in 1889 and about 5860000 lbs. in 1891, had fallen to 2961000 lbs. in 1895[2]). The exports returned after that date, *i. e.* after the occupation of Formosa by the Japanese, doubtless include some camphor grown in Formosa, so that they cannot be regarded as reliable figures for Japan proper. For this reason, we would only mention the following particulars: — In 1907—8, 1618 families were engaged in camphor production in Japan, and the production of crude camphor was 987922 lbs. In 1910—11, 2615 families produced 1394896 lbs.; in 1915—16, 4239 families produced 2117878 lbs.; in the following year, 4329 families only produced 2074113 lbs., and in 1917—18 only 3274 families were engaged in the industry, and the production fell to less than 1300000 lbs. — For 1919—20a yield of 4000000 kin (5291000 lbs.) was anticipated, and a return to the normal yield of 5000000 to 6000000 kin (6615000 to 7938000 lbs.) for the next year. It is not to be expected that any considerable share thereof will enter foreign commerce. In 1918, the Japanese industry consumed 9600000 lbs. of crude camphor, and in May, 1920 all export of crude camphor was prohibited, a limited amount of refined camphor being allowed to foreign refiners at a discount of 3 per cent. below the market price. In former years nearly all the camphor was exported, whereas in China the export was only one-fourth of the quantity produced.

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[1]) *Drug and Chemical Markets* 9 (1921), 1206. — [2]) Comp. also statistics in Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, page 473.

As stated already in previous *Reports*, the Japanese Monopoly Board had started since 1900 planting camphor trees on a large scale, hoping for a great success[1]). But in 1918 it is admitted that the expectations to be able to obtain camphor from the leaves had not been fulfilled and that the camphor obtained from young trunks was not satisfactory. The yield to be obtained from the planted camphor trees, even in another 10 to 15 years, will most likely not be so considerable either, as generally pretended. The trees will by then be about 35 years old, whereas the highest yield is not arrived at till they are 60 years old.

Formosa exported 6927000 lbs. of camphor in 1895, compared with 7860000 lbs. in 1913, and the following table shows the exports for the years 1915—1919.

Production and Export of Formosan Camphor

		to the United States	to Europe	to Japan
1915/16 . . .	10389521 lbs.	4211766 lbs.	1798277 lbs.	4379478 lbs.
1916/17 . . .	11506447 „	6525489 „	1726997 „	3253961 „
1917/18 . . .	7945890 „	4129027 „	1045345 „	2771518 „
1918/19 . . .	6137732 „	2055188 „	913021 „	3169523 „

According to *Commerce Reports*[2]), it is supposed that the camphor production in Formosa amounted to 6 million lbs., from April 1st 1920 to March 31st 1921, exceeding that of the previous year by 275000 lbs. The export, which in July 1920 amounted to 480000 lbs., rose till March 1911 to 600000 lbs. monthly. In the expectation that the celluloid industry will revive as soon as the present stocks will have been cleared, the Monopoly Board means to increase gradually the quantity of camphor produced. Already towards the end of the Chinese administration in Formosa, there existed a monopoly for camphor, but as it sustained considerable losses, owing to its reckless exploitation and inadequate methods of production, an own monopoly system was created for the island in 1899. In 1903 a joint Monopoly Act was passed for Japan and Formosa.

The number of camphor trees growing in the public and imperial forests of Formosa is estimated at 12 millions, said to correspond to 2½ (??) million cubic feet of wood. The other camphor trees in Formosa, from 100 years of age upwards, are supposed to represent 30 million cubic feet of wood, out of which 17500 tons of camphor and 12800 tons of camphor oil might be obtained[2]).

The Government spends 50000 yen annually for planting young camphor trees in Formosa. More than 30000 acres have been planted, whereas in Japan proper there are only 2000 acres with such plantations. The Government approved of a plan to plant 5000 *tsubo* (1 tsubo = 2.5 acres) with camphor trees annually for 11 years from 1918, to protect all the wild trees and to reduce the export as much as possible.

The production of camphor in Formosa is dealt with in two articles by H. J. Shepstone[3]) and A. B. Kirjassoff (*"Formosa the beautiful"*)[4]). The illustrations regarding the whole process of camphor production, as given in Kirjassoff's treatise, are specially interesting and instructive. As Shepstone reports, there are nine tribes in Formosa, all of which are hostile to each other, and the largest and most powerful is the Atayals, who number about 30000, occupying an area of 2500 square miles in the northern part of the island, much of which has never been explored. Head-hunting is the most glorious thing in their lives, and a lad is not an adult until he secures a human head. The seriousness

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[1]) Comp. *Reports* **1918**, 12; **1919**, 11. — [2]) *Deutsche Allgem. Ztg.* According to *Chem. Industrie* **44** (1921), 413. — [3]) *The World's Work*, **Oct. 1921.** As per *The Chemist and Druggist* **95** (1921), 568. — [4]) *The National Geographic Magazine* **37** (1920), 241.

of their attacks on the camphor-gatherers may be gauged from the fact that during 1914, when the statistics were last available, 187 of the collectors were killed and 190 wounded.

In order to reach the large tracts of camphor forests in the interior, it was essential to overcome the savages. The method employed was the establishment of a "guard line" all round the mountainous interior, with small military outposts at intervals, and this artificial frontier has gradually been extended, so that the turbulent natives are confined in a slowly-diminishing area. As this method was too slow, in view of the present state of the industry, the Japanese Government recently voted £ 1000000 to bring about a more rapid pacification of the savages, and troops have been sent in large numbers. The Formosan native must, therefore, quickly change his attitude towards the camphor-gatherers or suffer annihilation. The Government is anxious to improve the lot and condition of the natives and to provide education for their children.

Shepstone says that an average camphor-tree, with a basal circumference of 12 feet, will yield about 3 tons of camphor. The felled trees are chopped into chips and subjected to distillation on the spot. The chips are placed in a retort over boiling water, and, as the camphor vaporizes, it passes through pipes into submerged vats, which are so arranged that cool water from a mountain stream can run over them to accelerate crystallization¹). After the camphor has crystallized, the vats are opened, and the product is placed on wooden troughs to allow whatever free oil there may be to drain off. This oil will yield 90 per cent. of crude camphor in the process of refining. The crude camphor is packed in tins and carried down precipitous mountain paths on coolies' backs to the nearest railway line, whence it goes to the Government refinery at Taihoku.

There are 80000 stills scattered over Formosa. They are in the hands of Chinamen, whereas the tree-fellers are Japanese.

As the Philippine Islands apparently offer favourable conditions for the cultivation of camphor-trees, the Government has granted a large stretch of land for this purpose to an American company.

In Ceylon, Nock had begun in 1893 to cultivate camphor-trees in the Hakgalla Gardens, six miles from Nuwara Elya, at a height of 5600 feet. The tree thrives best at a height of 3 to 5000 feet on chalky soil, also containing potash. As it is not sensitive with regard to wind, it is often found as a sort of wind-screen for tea plantations²). The twigs and branches yielded 2.7 to 3.4 per cent. of camphor oil and 0.75 to 1 per cent. of camphor. The output amounted to 143 to 190 lbs. of camphor. Bamber and Willis stated in 1910 that the cultivation of camphor-trees was successful in Ceylon, if they were plated in rows facing the direction of the predominating winds, on sandy clay often watered by rain. Within five years they attain a height of 18 to 20 feet.

It seems that at least three different kinds of camphor-trees are cultivated in the West-Indies. A tree in St. Vincent, supposed never to have bloomed, over 100 years old, and which had been determined in Kew as *Cinnamomum Camphora*, var. *glaucescens*, yielded on distillation of the wood only oil, but no solid camphor. Another, also inferior kind in Trinidad and Dominica is conspicuous by its reddish shoots and leafstalks and its oval leaves which, on being crushed, smell of turpentine oil. However, there are also trees on these two islands, as well as in Jamaica, the leaves of which yield 1 per cent. of camphor or more.

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¹) It is to be seen from this description that it refers to an improved kind of the usual Chinese distilling apparatus, originally employed in Formosa. In Japan proper the production of camphor has been further improved. (Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, page 456.) — ²) Comp. *Report* 1918, 15.

Cinnamomum Camphora is cultivated all over Queensland, where another new species occurs, *Cinnamomum Oliveri,* which is said also to contain camphor.

In New South Wales, the fresh leaves of a tree, 15 years old, yielded 1.02 per cent. of camphor.

A remarkable camphor-tree is found on an island in the Lago Maggiore. When eight years old, its trunk was 1 foot in diameter and had the extraordinary height of 90 feet. Camphor-trees also grow in Buenos Aires, the Canaries and Madagascar. On the latter island the wood of trees over 50 years old is used as building material.

The first camphor-tree plantation in Satsuma, Florida, put 10000 lbs. of camphor on the market since the beginning of this year. The product is stated to be equal in every respect to the Japanese refined camphor. Two companies are said to have 2500 acres each under cultivation. A third company has been granted permission to start a large plantation in Texas[1].

According to the *Revue agricole de l'Afrique du Nord*[2] several hectares in the Doumia Woods (Algeria) have been planted with camphor-trees in 1919. The success obtained there, as well as in the districts of Algiers, Blida, Boudjia, El Miliah and El Hanser, are supposed to induce the Government to substitute more and more the camphor tree to the cork-oak in the coastal regions of Algeria, especially in the moist East, where the cork of the oaks is always damp and therefore of no value. According to Trabut it would be possible to obtain from a camphor-tree plantation, when 25 years old, 300 kilos each of camphor and camphor oil per hectare[3].

According to S. T. Dunn[4], it is stated that the direct cause of the presence in the camphor-tree of essential oil of varying constitution and quantity is to be found probably in the formation within the plant of terpentinol ($C_{10}H_{16}$)[5], which is gradually changed by the activity of the living cells into camphor ($C_{10}H_{16}O$). As this oxidation progresses, different compounds appear, and it is by their admixture in the products of distillation that all the different oils and finally camphor itself is formed. "If this theory is accepted", Mr. Dunn observes, "it is not surprising to find that the yield of camphor varies from month to month." Cases are cited to prove that in certain countries, notably Japan and Formosa, much more camphor is obtained from camphor-wood cut in the cool season than from that cut in the summer. Any other circumstance affecting the healthiness and cell activity of *Cinnamomum Camphora* will, it is pointed out, on the above theory, also affect the yield of camphor. It is suggested, for example, that fungal disease of the wood may have a deterent effect on the production of camphor, and it is also noticed, in this connection, that the climatic conditions of North Formosa seem to favour a plentiful production of solid camphor, whereas in the South, many trees yield little solid camphor, but large quantities of Sho oil and Yu-yu oil, the trees being known to the Japanese as Sho-gyu and Yu-yu, respectively[6]. In the climate of Florida the same species produces solid camphor mixed with an oil differing from the Japanese oils in its low percentage of safrole. Remarkable variations of camphor content in the leaves of trees growing under different conditions of shade and soil have also been recorded[7]. Experiments in Kew have shown that, apart from two slight colour

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[1] *Journ. Soc. Chem. Ind.* **40** (1921), R. 388. — [2] *Parfum. moderne* **14** (1921), 212. — [3] Comp. *Report* April **1908**, 23; *Bericht* (German ed.) **1920**, 13. — [4] *Bull. of Miscellaneous Information* no. 4, **1921**. As per *Perfum. Record* 12 (1921), 323. — [5] The designation of "terpentinol" for hydrocarbons $C_{10}H_{16}$ is, of course, absolutely incorrect. — [6] According to K. Nagai, the Shô-Gyu and the Yu-Ju trees, the botanical origin of which is still unknown, are not identical with *Cinnamomum Camphora.* The Yu-Ju oil has a great resemblance with camphor oil. Comp. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd edition, vol. III, page 672. — [7] Comp. also *Report* **1918**, 15.

indications, no visible varietal characters can be found in any part of the tree to separate "camphor" trees from "oil" trees. Dunn suggests the following lines of improvement for plantations of camphor trees: (1) Seeds should be secured from trees known to produce camphor, (2) suitable climate and soil should be selected, (3) saplings must be planted so that they may be clipped conveniently; (4) the best months for clipping must be ascertained by experiment, as observations show considerable changes in the camphor content of the leaves as the growing season advances.

Cananga Oil. — It is reported that the distillation of this article in Java is no longer remunerative at the present price obtained for it in Europe, *i. e.* 10 to 12 Dutch Florins per kilo, especially because the producers lack cheap fuel. According to our informants, the distillation stopped almost completely in 1921, all the oil shipped being of 1920 production. As the wages for the collectors of the flowers have doubled since the war, the distillers prefer waiting until they know the consumers' attitude with regard to the higher prices that are to be expected.

Caraway Oil. — The Dutch caraway market was very firm throughout the year 1921. Owing to the small crop (only 15000 bales, *i. e.* even less than in the previous year), the prices rose during the summer up to about 17 florins, but towards the end of the year they went down a little, to 16 florins, as there was no very keen demand. The stocks of old caraway, which had agglomerated considerably, as we reported previously, have gradually been disposed of, so that the average quality was better than in 1920. One expects very little of the 1922 crop, in fact less than the year before, as the seedlings from spring 1921 had to be ploughed under, owing to the drought in autumn. The quantities available up to the next crop but one, *i. e.* in August 1923, will most likely prove insufficient for the world's requirements, so that very high prices are to be expected.

As regards the caraway market in 1920, some information from the Dutch Board of Agriculture is now available¹), from which we gather that the area under cultivation was 971 hectares. The crop was small, but there were still considerable stocks of old seed. There was but little business with Central Europe; England and the United States, however, took again the usual quantities. The prices ranged from 22 down to 15 florins. Owing to high rent, big wages and expensive manure, the cultivation is said to have become unprofitable, so that it is to be feared that it will be given up. The exports in 1920 totalled 3767 tons to the value of 1412000 florins.

There were fairly considerable offers of East-Friesian and East-Prussian caraway, but unfortunately the largest part by far was exported, as the prices paid abroad were tempting. Only comparatively small lots were available for distillation in the country. It is to be regretted that the German Government have not realized so far, how necessary it is to stop the exports of caraway seed. On the other hand, one is pleased to see that the German farmers have given far more attention to the cultivation of caraway and that the success is visible already.

Oil of Cathetus fasciculata. — In the course of this year we received two samples of the so-called *Bruyère* oil, distilled in Annam (Further India) from the *Euphorbiacea Cathetus fasciculata,* Lour. As the oil is but little known, we think the following particulars will be of interest: — The samples were pale yellow and yellow, respectively,

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¹) *Verslag omtrent Handel, Nijverheid en Scheepvaart van Nederland gedurende* **1920.**

and their odour recalled cajuput oil, d_{15° 0.8826 and 0.8905, α_D −2°9′ and −5°26′, n_{D20° 1.47730 and 1.47926, acid v. 1.1 and 1.8, ester v. 4.3 and 4.2, soluble in 0.5 and 3.5 vols., respectively, of 90 per cent. alcohol. Of 80 per cent. alcohol even 10 vols. were insufficient for a solution.

These properties tally on the whole with the indications regarding *Bruyère* oil in Gildemeister and Hoffmann, *The Volatile Oils,* 2nd edition, vol. III, page 146.

Chamomile Oil. — According to an English periodical[1], oil of chamomile is a suitable solvent for platinum chloride. It is said to be used for this purpose in the glass and porcelain industries, in order to coat vessels with platinum.

Chenopodium Oil. — See Wormseed Oil, p. 80 of this *Report.*

Cinnamon Oil, Ceylon. — The demand for cinnamon oil and, in a still higher degree, for cinnamon leaf oil has increased considerably during the last years. The latter can be obtained in a satisfactory quality from Ceylon, the Seychelles and Mauritius, whereas it seems to be impossible so far to distil a good bark oil from raw material of other origin than Ceylon, although it is reported that cinnamon bark from the Gold Coast has yielded in the last years valuable oils of agreeable odour[2]. The area planted with cinnamon trees in Ceylon has decreased continuously, as other plants, like caoutchouc-trees and coconut palms pay better. The latest official estimate[3] of the total area under cinnamon is about 35000 acres, as compared with 48000 acres in 1909. The cinnamon gardens of Ceylon are situated chiefly in the Southern and Western Provinces of the island. The following tables give details of the exports from Ceylon: —

Annual average export of cinnamon bark from Ceylon during the decades

1841 to 1850	529 461 lbs.	52 497 £[4]
1871 „ 1880	1 274 668 „	64 649 „
1881 „ 1888	2 088 232 „	107 604 „
1901 „ 1910	5 565 684 „	171 395 „
1911 „ 1920	5 155 470 „	134 760 „

Exports from Ceylon

Year	Cinnamon bark[5]		Cinnamon bark oil[6]		Cinnamon leaf oil	
1909 . . .	6 501 040 lbs.	181 913 £	—	—	—	—
1910 . . .	6 306 060 „	186 219 „	90 710 oz.	1618 £	76 008 oz.	519 £[4]
1911 . . .	5 773 140 „	139 086 „	49 502 „	1131 „	63 600 „	453 „
1912 . . .	5 945 632 „	188 992 „	65 972 „	1417 „	34 020 „	186 „
1913 . . .	5 140 800 „	160 908 „	16 112 „	715 „	52 092 „	354 „
1914 . . .	4 080 272 „	107 777 „	10 129 „	673 „	36 936 „	228 „
1915 . . .	6 451 984 „	133 178 „	36 343 „	1698 „	64 692 „	1061 „
1916 . . .	5 012 896 „	83 713 „	62 132 „	1620 „	120 874 „	1809 „
1917 . . .	3 328 192 „	64 518 „	78 438 „	2655 „	95 091 „	1199 „
1918 . . .	4 187 680 „	89 900 „	62 283 „	5109 „	258 020 „	5048 „
1919 . . .	7 700 560 „	246 393 „	66 773 „	5655 „	299 928 „	6274 „
1920 . . .	3 933 552 „	143 141 „	73 246 „	2572 „	365 976 „	5553 „

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[1] *Perfumer's Journ. & Essential Oil Recorder.* As per *Deutsche Parf. Ztg.* 7 (1921), 95. — [2] Cf. *Bericht* (German) 1920, 66. — [3] *Bull. Imp. Inst.* 19 (1921), 319. — [4] Converted from rupees at the rate of Rs. 15 = £ 1. — [5] Cinnamon bark includes quills and chips. — [6] The cinnamon bark oil exported from Ceylon was as a rule strongly adulterated with cinnamon leaf oil.

Before the war Germany was, as a rule, the largest buyer of both quills and chips; other important countries to which the bark was shipped being the United Kingdom, Spain, Holland, Italy, the United States and Belgium. In 1920 Germany again became an important buyer 218 736 lbs. of quills and 134 176 lbs. of chips, against 4928 lbs. of quills in the year before, in that year the United States being the chief buyer of quills.

The best cinnamon is grown in Ceylon in a very sandy clay or fine white quartz sand, with a good rich sub-soil, at altitudes of less than 1500 feet, in the strip of land 12 to 15 miles wide, on the south-west coast, between Negumbo, Colombo and Matura. The tree is usually grown from seed in nursery lines and transplanted when 3, 4 or 12 months old. Sometimes it is propagated by cuttings of very young three-leaved shoots, or by layers. Adult trees flower in May and fruit in July; and, unless bagged for seed, the entire crop of fruit is liable to be eaten by birds. The ripe fruit is heaped in the shade until the pulp turns black and rots, when the seed can be removed by trampling; the seed is washed and dried in the shade before sowing. — Cattle, goats and squirrels nibble the young shoots; but otherwise cinnamon is not very liable to animal or vegetable pests. *Pestalozzia cinnamomi,* Raciborski, is a minute leaf and twig fungus; and the "pink disease" (*Corticium salmoni-color,* B. and Br.), a wet season disease, well known as attacking Para rubber, forming a pink crust on the stem and destroying the cambium, a sign that the trees are over-crowded, also occurs and can be dealt with by spraying with Bordeaux mixture and excising and burning affected parts.

In order to obtain the bark, the shoots, usually two years old, averaging 3 to 4 feet in length and 0.5 to 0.75 inch in diameter, are cut in May or November, when the sap moves and facilitates peeling. The slips of bark are heaped together and covered over for a day or two, so as to undergo, perhaps, a slight fermentation¹) which facilitates the scraping off of the epidermis and pulpy hypoderm in the process known as "piping". The slips of bark contract into pipes or "quills", which are packed one inside the other, cut square and of uniform length, dried in the shade and ultimately in the sun, and eventually made up into bundles of 100 lbs. weight. The prunings and waste pieces obtained in peeling are known as cinnamon chips. They have only been exported from Ceylon since 1867 and have been used since 1872 chiefly for distilling cinnamon oil²).

There is no evidence of the cultivation on any commercial scale of the true cinnamon *(Cinnamomum zeylanicum)* in India, though it may be represented as a wild tree in the Western Ghats. But various barks and twigs are sold as *Cassia lignea* originating from other Cinnamomum specias, such as *C. Tamala,* Nees et Eberm., *C. obtusifolium,* Nees (closely allied to *C. Cassia*, Blume), *C. iners,* Wight³) (according to Thwaites and Ridley only a coarser form of *C. zeylanicum,* like *C. nitidum,* Blume, and some others)⁴) and *C. macrocarpum,* Hook. fil. The essential oils of these drugs are used partly for adulterating the genuine cinnamon oil, partly in the soap industry.

Cinnamon trees were introduced into Seychelles with other species, about 1775, from the Dutch East Indies, and were for a time cultivated in the Royal Gardens at Mahé. The trees spread through the forests and were neglected until 1908, in which year 1202 tons of bark were exported. At the same time distillation of oil from the bark of the wild trees was commenced. The bark differed but little in appearance

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¹) The fresh white bark turns red on drying, owing to the formation of phlobaphene. A fermentation is not very likely to occur. — ²) Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd edition, vol. II, p. 419. — ³) According to the *Index Kewensis, Cinnamomum iners,* Wight, is identical with *C. zeylanicum.* — ⁴) Dymock, *Pharmacographia Indica,* 1893, vol. III, p. 208.

from that of the trees cultivated in Ceylon[1]), but it was never handled so carefully, never had the fine aroma of Ceylon cinnamon[2]) and in consequence never fetched so good a price. The exports of bark from Seychelles for the years 1908—1919 are shown in the following table:—

1908	1202 tons	1915	189 tons
1909	1044 „	1916	184 „
1910	731 „	1917	1 „
1911	964 „	1918	*nil* „
1912	1098 „	1919	275 „
1913	698 „	1920	185 „
1914	589 „		

Prior to 1915 most of the bark was shipped to Germany, Holland being the next most important customer. In 1915 and later years the bulk went to the United Kingdom. After twelve stills had been installed in 1915 for the distillation of cinnamon bark and leaf and lemongrass oils, the exports increased sevenfold within three years. During the war the development of the industry was hampered by the impossibilty of obtaining modern machinery for steam distillation from Europe, but a Chinese settler set the example of building a small still of wood and iron obtained locally for direct fire distillation: his example was followed by many small-holders. On samples being submitted to the Imperial Institute, it was found that there was not much difference between the oils obtained by steam distillation and those from direct fire distillation. The high price reached by cinnamon leaf oil encouraged the manufacturers to devote themselves mainly to this oil, as is shown by the following table of exports, and during 1920 there were 44 distilleries at work (total production 24430 litres)[3]), as against 12 in 1915.

Export of Cinnamon Oils from Seychelles.

	Bark oil		Leaf oil	
1911	1 l	0,2 £	212 l	56 £
1912	—	—	1 543 „	338 „
1913	—	—	3 054 „	799 „
1914	—	—	8 406 „	2 320 „
1915	99	73 „	9 587 „	2 505 „
1916	1834 „	1041 „	15 669 „	4 484 „
1917	91 „	171 „	14 175 „	4 317 „
1918	131 „	262 „	12 731 „	5 111 „
1919	27 „	46 „	24 430 „	11 634 „
1920	—	—	39 507 „	26 029 „

The price of cinnamon leaf oil having fallen from 10 rupees to about Rs. 3 to Rs. 4 per litre in 1920[4]), little has been manufactured since, so that the exports for 1921 will show a decline.

Up to 1911 no difference was made in Seychelles between bark and leaf oils. The exports of "cinnamon oil" were 285 litres in 1908, 12 litres in 1909 and 124 litres in 1910.

A number of trees having been planted near Malacca, a small quantity of quills were prepared in 1851 by Sinhalese convicts, who were professional cinnamon peelers, and sent to England, but although, considering that the bark was cut at the wrong season and from neglected trees, the report was favourable and the bark was paid

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[1]) Cf. *Reports* April 1910, 35; April 1911, 43. — [2]) Cinnamon oil from Seychelles differs also from the Ceylon product in that its content of cinnamaldehyde is lower and that it contains camphor. *Report* November 1908, 42. — [3]) As per *Heil- und Gewürzpfl.* 4 (1921), 127. — [4]) *Perfum. Record* 12 (1921), 415.

fairly well, the cultivation was not proceeded with, probably on account of the low prices which have since prevailed. — Various other species of *Cinnamomum* occur in a wild state in the Malay region, some of which, such as *C. tavoyanum*, are akin to *C. Cassia*, whilst others, such as *C. Parthenoxylon*, are more allied to *C. Camphora*. *C. Culilawan*, Blume, the clove bark[1] of the Malays (*Kulit* = bark, *Lawang* = clove) is a native of both the Peninsula and the islands. The calyces of the fruit are used locally in medicine and curries under the name of *"bunga lawang"* (clove flowers).

The cultivation of *Cinnamomum zeylanicum* was introduced into the Dutch East Indies (Java) in 1825, as it seemed with success in the beginning. It resulted afterwards, however, that the fine quality of the genuine Ceylon cinnamon could not be attained, and from 1865 the cultivation gradually died out. The tree is now grown only on a small scale on a few European estates. — A trifling quantity of bark is derived in Java from *C. Cassia* and the rest from *C. Burmanni*, Blume[2], a tree growing wild throughout the Malay archipelago. It is a slender tree occurring chiefly in the mountains, and the bark is stated to improve in quality the greater the altitude at which it is grown. The better qualities of bark are from the trunk, the second quality, which is lacking in flavour, being derived from the thicker branches. The United States has been the chief purchaser of the product, Holland taking the bulk of the remainder.

Total Exports of Cinnamon Barks from the Dutch East Indies (Padang, Java and Macassar) in the years from 1908 to 1912: —

1908 . . . 752 tons = 22916 £
1909 . . . 1016 „ = 32833 „
1910 . . . 1297 „ = 37333 „
1911 . . . 1922 „ = 22250 „
1912 . . . 1032 „ = 23666 „

Both *Cinnamomum zeylanicum C. Cassia* have been successfully grown in Fiji from seed, and the bark and the leaves distilled on a small experimental scale at Nasimu[3]. The cinnamon was planted in 1906, and is stated to have become quite naturalized, the seeds being distributed through the forests by pigeons.

As to the West Indies, cinnamon was found by Captain Marshall in 1782 in St. Domingo. It was sent to Jamaica and has since been grown in the island, but not on any considerable scale. A bark frequently known in the drug trade as "wild or white cinnamon", is that of *Canella alba*, Murr., a *Winteranacea*, in no way related to the true cinnamon. It is a native of Florida and the West Indies, and has been known as "Jamaica Winter's Bark" and "Jamaica Cassia lignea" but is now shipped mainly from New Providence in the Bahamas under the names of "White Wood Bark" or "Cinnamon Bark".

Some data from an English source[4] as to the history of cinnamon barks[5] which, as it is well known, belong to the oldest spices, will certainly interest our readers. According to D. Hanbury none of the cinnamon of antiquity was derived either from *Cinnamomum zeylanicum* or from Ceylon. The very name "cinnamon" from the Arabic *"mama"* or Greek *"amomum"* (meaning spice) and the prefix *"chini"*, Chinese, which persists in the Persian and Hindustani *"Darchini"*, suggests the Chinese origin of the drug, and under the name *"Kwei"*, which forms part of several Chinese place-names,

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[1] The essential oil of this bark contains 62 per cent. of eugenol and some methyl-eugenol. Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, p. 439. — [2] As to oils from the bark of *Cinnamomum Kiamis*, Nees = *C. Burmanni*, Blume, see Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, p. 438. — [3] *Rept. on Agric., Fiji*, **1911**, p. 7; **1918**, p. 6. As per *Bull. Imp. Inst.* **19** (1921), 338. There are no further particulars in this publication. — [4] *Bull. Imp. Inst.* **19** (1921), 321. — [5] Cf. also Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 125.

cassia is mentioned in the earliest Chinese herbal, said to have been written in 2700 B.C. The mention of *"Tien-chu kwei"*, that is Indian cassia, in the *Pen-tsao*, written in the eighth century may refer to bark produced in Malabar. The mention of two spices or perfumes, cinnamon and cassia, in the older books of the Old Testament and in the earliest Greek works on medicine, as nearly allied but of different value, may have only referred to two qualities of what we should now call cassia, this latter name — originally *"casia"* — being related to the Hebrew *"ketzioth"*, meaning "stripped off". The barks were originally brought to Europe — that is to the Levant — by Phœnicians, who obtained them from the Arabs, and the ancient notion that they were derived from a *"regio cinnamomifera"* in Somaliland may have been merely an error arising from this trade passing through several hands or part of the common characteristic system of trade mystification. The full Arabic name *"Kirfat-et-darsini"*, bark of the Chinese tree, shortened into *"Kirfah"*, persists as *"Kalfah"*, the existing Bombay name for Malabar cassia. As Sir Emerson Tennent pointed out, there is no mention of cinnamon as a product of Ceylon prior to the Arab writer Kazwini, about A. D. 1275, and the Minorite friar, John of Montecorvino, about 1293; and Hanbury makes the highly probable suggestion that the Chinese, who were acquainted with *C. Cassia*, a very similar tree, and who traded with Ceylon and the coast of Malabar, were concerned in the discovery of the value of the Ceylon bark. The Chalias, the caste to which the peeling and preparation of cinnamon bark is now restricted in Ceylon, are said to have emigrated from India in the thirteenth century; and in the following century Mohammedan writers were well acquainted with Ceylon cinnamon and the difference between it and Chinese and Indian cassia. One of them, writing in 1368 of *"Darchini"*, says "the best is that which comes from Ceylon", while the best Chinese cassia *("salikheh")* is, he says, thick, reddish, a little bitter and astringent, but sweeter than Indian Kirfah which "tastes like cloves".

The Portuguese, arriving in Ceylon in 1505[1], found the cinnamon in a wild state, and exacted a tribute of 250000 lbs. of bark annually from the Sinhalese king. Garcia da Orta, about the middle of the same century, speaks of Ceylon cinnamon as worth four times as much as that from Malabar, and the Portuguese occupation of Ceylon in 1536 is stated to have been accomplished chiefly for the sake of the cinnamon. After the Dutch conquest in 1656 the Government monopoly of the export of bark was strictly maintained, but it was under the Dutch auspices that, about 1770, the cultivation of the tree was commenced. The entire European demand, stated to have been about 400000 lbs. a year, was then supplied from Ceylon; and, after the British conquest in 1796, the annual production, during the monopoly of the East India Company, which lasted until 1833, did not exceed 500000 lbs. The Dutch began the cultivation of the tree in Java in 1825, and, while a heavy export duty was imposed on Ceylon bark until 1853, the competition of Javanese bark and of Chinese cassia told upon the Ceylon industry.

Cinnamon barks and chips from Madagascar, received by Roure-Bertrand Fils[2], yielded on steam distillation 0.17 per cent. of essential oil of the following properties: d_{17° 0.9715, d_{15° 0.9731, $\alpha_{17^\circ} - 5^\circ 49'$, acid v. 2.49, aldehyde content 48 per cent.; incompletely soluble in 70 per cent. alcohol, soluble in 1 vol. of 80 per cent. alcohol; on addition of more alcohol, turbidity which disappeared again, however, when the quantity of alcohol reached 10 volumes.

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[1] Vasco da Gama reached the coast of Malabar already in 1498. — [2] *Bull. Roure-Bertrand Fils*, October 1921, 35.

From the distillation water 0.3 per cent. of an entirely different oil could be extracted with light petroleum: d_{17° 1.0281, d_{15° 1.0297, α_{16° — 2° 2′, acid v. 2.49, aldehyde content 82 per cent., soluble in 1.75 vol. of 70 per cent. alcohol and in 0.75 vol. of 80 per cent. alcohol, further addition of alcohol caused slight turbidity. A mixture of both oils had the following constants: d_{17° 1.0075, d_{15° 1.0091, α_{17° — 3° 23′, acid v. 2.49, aldehyde content 70 per cent., soluble in 2 vols. of 70 per cent. alcohol; slight turbidity on further addition of alcohol. The oils referred to were amber-yellow, their odour reminded one somewhat of Ceylon cinnamon oil, but they did come near the quality of the latter.

Cinnamon Leaf Oil. — Little has been published so far on cinnamon leaf oil from South Kanara; the more interesting therefore what C. K. Menon[1]) says about it. The cinnamon tree, *Cinnamomum zeylanicum,* Nees which according to Tschirch occurs in the south-west of British India in very different forms[2]), all belonging to the same species, however, grows abundantly in the coast district of South Kanara at elevations varying from 100 to 700 fest — and fairly up to 3500 feet on the Ghat slopes. The local distillers distinguish four kinds of trees from the taste of the leaves, *viz., "mitta"* (sweet), *"pickka"* (insipid), *"tej"* (pungent), and *"kadira"* (bitter). They collect the leaves only of the last two for oil extraction, the first two are reported to be useless for this purpose. In Ceylon the leaves are macerated in sea-water and subsequently distilled, but in South Kanara the first operation is not carried out. In that district the rude apparatus for distilling the leaf oil consists of three earthen pots, serving respectively as boiler, covering pot and receiver, with two short bamboo tubes to conduct the steam from the boiler to the condenser. The large earthenware pot which acts as the boiler is placed over a furnace; water is poured into it to a depth of 9 inches. Fairly matured green leaves are packed into it. A small earthenware pot is kept with its mouth down over the boiler, the joint being well plastered with clay and cow-dung mixed. A small bamboo tube, about a foot long and half an inch in diameter, is thrust through a hole in the top of the upper pot. To the free end of this tube, another about three feet in length is attached, the two joints being wrapped up in cloth and plastered well with the clay mixture. The longer tube is led into the condenser, fixed in a tank containing cold, muddy water. A thick wet cloth is spread over the mouth of the condenser, and around the bamboo tube. The muddy water is replaced as it gets heated. The water in the boiler is heated to boiling point; the steam and the extracted oil are condensed against the cool sides of the condenser. The oil being heavier than water, sinks to the bottom.

The working season lasts only from November to March, after which the young leaves appear, and these would not yield sufficient oil to repay the labour. In North Mangalore Forest Division of the South Kanara district cinnamon areas in the unreserved lands are divided into working circles; each one is intended to provide leaves for five stille annually during the working season. The number of local distillers is fixed, and each working circle is auctioned to a single individual.

Menon suggests that cinnamon growth should be concentrated within small and compact areas, instead of continuing the present system. The plant can easily be grown from seed. The average annual production is about 25 tins of oil (1 tin = 24 bottles = 18 litres), which is sent to Bombay, the chief market for South Kanara oil.

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[1]) *Perfum. Record* 12 (1921), 31. — [2]) Cf. also page 20 of this *Report.*

Citronella Oil from Java. — The Java export figures from January up to the end of November 1921 have now been published as follows: —

Holland	30373 kilos
Great Britain	8356 "
Germany	10040 "
France	26331 "
United States	92118 "
Singapore	8391 "
China	8235 "
Japan	64029 "
Other countries	889 "
	248762 kilos.

The exports in the last three years totalled: —

1918 = 228000 kilos
1919 = 528500 "
1920 = 434500 " ,

the separate figures being: —

Destination	1918	1919	1920
Holland	—	233000	124000
Great Britain	—	91000	75000
France	—	69000	80000
Switzerland	—	6000	—
United States	84000	85000	76000
Singapore	46000	24000	44000
Hong Kong	5000	6000	1000
China	4000	2000	9000
Japan	81000	7000	19000
Australia	1500	3000	4500
Germany	—	—	—
Other countries	6000	1000	—

The low figures for Germany are explained by the fact that she had no direct steamer connection with the Dutch Indies during the period referred to. Her real consumption is contained in the figures given for Holland.

Australia bought as long as there was little or no Ceylon oil available. Singapore and Hong Kong are only places of transit.

As it will be remembered, the total export of Java citronella oil was 426000 kilos in 1916 and 515000 kilos in 1917. The diminution by nearly 300000 kilos in 1918 was due to shipping difficulties, which were overcome only gradually in the course of 1919. Since then the costs of production have risen considerably, owing to the upward movement of the wages in 1919 and 1920. Besides, various factories of medium size have become State property by repurchase or expropriation on account of older claims and they have been closed, as such factories do not lend themselves to be managed by the State. A somewhat correct estimate of the total production can only be based on the average export figures of several years, the available data regarding the area under cultivation being inaccurate. In competent quarters the average annual production is estimated at 350000 kilos, for the distillation of which 60000 tons of citronella grass would be required, supposing a yield of 0.6 per cent. The total production in 1921 is stated to have been about 320000 kilos.

Of the above-mentioned shipments of 248762 kilos for the time from January to November 1921, only 82000 kilos were forwarded during the first six months, as the prices then left very little profit. Business revived as soon as the market improved.

The production is said to have gone down considerably during the summer months, owing the extraordinarily dry weather.

A citronella oil from the Seychelles of the year 1918, investigated by the Imperial Institute[1] had the following constants: — $d_{15^\circ}^{15^\circ}$ 0.881, α_{D20° — 28° 30′, soluble in 1.7 vols. 80 per cent. alcohol at 20°, turbidity with 10 vols., insoluble in 80 per cent. alcohol at 15°. Total geraniol (all acetylizable constituents calculated as geraniol) 52.2 per cent., geraniol 27.5 per cent., citronellal 24.7 per cent.[2]. Compared with other citronella oils, the sample resembled somewhat the Ceylon product. The citronella grass, from which the sample in question had been distilled, had been imported from Ceylon to the Seychelles.

Clove Oil. — For the time being there are no special reports on the Zanzibar clove market. — Only 10 to 15 tons of the Madagascar cloves come from the mainland, the larger part being gathered on the island St. Marie, situated near the north-east coast. The exports, chiefly to France, were 143 tons in 1918 and 499 tons in 1919. Although the shipments in December 1920 amounted to 87 tons, the whole 1920/21 crop totalled only 20 tons. The prospects for 1921/22 are said to be good[3].

Oil of Coleus amboinicus. — According to F. Weehuizen[4], the leaves of *Coleus amboinicus,* Lour.[5] (*C. carnosus,* Hassk.), a labiata indigenous in Java, contain an essential oil (0.055 and 0.021 per cent.), in which the presence of carvacrol could be proved.

Copaiba Balsam Oil. — In order to avoid the often disturbing influence of concentrated sulphuric acid, J. B. Luther[6] carried out Turner's reaction for the determination of gurjun balsam oil in copaiba balsam oil as follows: — After having added 1 drop of a 10 per cent. solution of sodium nitrite to a solution of 4 drops of the oil in 1 cc. of glacial acetic acid, this was mixed at once with 2 cc. of glacial acetic acid containing 5 per cent. by volume of concentrated sulphuric acid. The presenee of gurjun balsam is revealed at once by a violet colour. Copaiba balsam turns red within a short time[7].

Coriander Oil. — Thuringian coriander was on the market in fairly considerable quantities, but the prices asked for were so high that our industry bought with the greatest reserve. The depreciation of the Mark caused in this case too that nearly the whole production was exported at high prices to the detriment of the home industry, for in the end the manufacturers of essential oils had to buy at export prices in order to replenish their stocks. It seems, unfortunately, that the Government little grasps the situation for, as with caraway and fennel, no reply has been given to a motion to stop the export.

In order to ascertain something about the effect of bleaching on coriander, J. A. Baker[8] treated the drug with sulphur dioxide. It was found through quantitative experiments that the action of a 1 per cent. solution of sulphur dioxide during one minute was quite sufficient to bleach coriander. This process answered better than a twenty-four hours' dry treatment of the seeds with double the quantity of sulphur dioxide. Whereas unbleached coriander yielded on steam distillation 0.185 per cent. of essential oil, the aqueous distillate of the bleached drug smelled of sulphur dioxide

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[1] *Bull. Imp. Inst.* 18 (1920), 338. — [2] It is not said how the determination was carried out. — [3] *United States Commercial Reports* **1921**. As per *Journ. Soc. Chem. Ind.* **40** (1921) R. 235. — [4] *Recueil Trav. Chim. Pays-Bas et Belgique* **37** (1918), 355. As per *Angew. Botanik* **3** (1921), 107. — [5] According to the *Index Kewensis Coleus amboinisus* is identical with *C. aromaticus,* Benth. — [6] *Journ. Assoc. Off. Agric. Chem.* **41** (1921), 422. As per *Journ. Soc. Chem. Soc.* **40** (1921), A. 488. — [7] Comp. also Gildemeister and Hoffmann, *The Volatile Oils,* 2nd edition, vol. II, page 620. — [8] *Journ. Americ. Pharm. Assoc.* **10** (1921), 453.

and contained no oil at all. Even upon cohobation of the aqueous distillates no oil was obtained. The distillate, however, then had a very pleasant odour.

The hitherto undecided question, whether bleached coriander is found on the market, could therefore, it seems, be solved with the aid of distillation. As far as our own experience with drugs goes, we have only found bleached hops and orris root, which of course were unfit for distillation.

Oil of Costus Roots. — In 1916/17 the Kashmir State Forest Department realized Rs. $3^1/_4$ lakhs revenue from the export of costus roots, 4.524 maunds of 82 lbs. being marketed[1]).

Cubeb Oil. — A sample of this oil was examined by C. T. Bennett[2]) and was found to lack the characteristic taste and odour usually associated with this oil. The physical characters answered the requirements of the British Pharmacopœia (d 0.922; $\alpha - 38^\circ$; n_{D25° 1.4965; 75 per cent. distilled between 250 and 280°). On adding a few drops of nitric acid to a solution in glacial acetic acid, the oil gave a distinct violet coloration, as is the case with oils containing gurjun balsam oil. On fractionation, the lower-boiling fractions showed a higher optical rotation than usually observed, the higher-boiling portions, however, which gave the gurjun balsam reaction, had a lower and more normal rotation. Further investigation revealed that the oil had been distilled apparently from genuine, but small and immature fruits of *Piper Cubeba,* whilst the Ph. Brit. requires that only fully-grown fruits should be employed.

Curcuma Oil. — From this oil, $d_{4^\circ}^{19^\circ}$ 0.9692, $d_{20^\circ} + 0^\circ 21'$ (in a 25 mm. tube), S.V. Hintikka[3]) obtained, on boiling with sodium ethylate, and after repeated distillation a pale yellow oil turning rapidly dark (b. p. 110 to 115° [8 mm.]) which on treatment with hydrochloric acid and washing with water boiled at 115 to 116° (10 mm.); $d_{4^\circ}^{19^\circ}$ 0.9481; n_D 1.50543. From this product, two semicarbazones were obtained, m. p. 129° and 153 to 154°, which furnished the following ketones: — *a)* b. p. 116 to 118° (10 mm.), $d_{4^\circ}^{19^\circ}$ 0.9493, $\alpha_{20^\circ} + 8^\circ 30'$ (25 mm. tube), n_D 1.50177; oxime, b. p. 160 to 161° (15 mm.); *b)* b. p. 122 to 124° (15 mm.), $d_{4^\circ}^{19^\circ}$ 0,9479, $d_{20^\circ} + 6^\circ 40'$ (25 mm. tube), n_D 1.49951. Since the letter ketone yielded, on treatment with semicarbazide, semicarbazones, m. p. 153 to 154° and principally with m. p. 125°, the two ketones were considered to be identical. The difference in the constants of the ketone are explained by its great tendency to oxidize. The combustion of both semicarbazones pointed to the formula $C_{10}H_{18}O$ of the ketone.

On oxidizing the crude ketone (not treated with hydrochloric acid) with potassium permanganate the author obtained a ketone (semicarbazone, m. p. 203 to 204°) which appeared to be identical with Rupe's[4]) *p*-tolylmethylketone, in addition to a substance which, on heating beyond 300°, was decomposed without previous melting (terephthalic acid?). When treated with a hypobromite, the ketone yielded a small quantity of a body melting at 33 to 34° (curcumic acid?).

Erigeron Oil. — The abundant occurrence of *Erigeron canadensis,* L., in the neighbourhood of Miltitz induced us to distil this well-known weed.

The whole plant, when just beginning to flower, yielded 0.264 per cent. of oil of the following constants: d_{15° 0.8720, $\alpha_D + 53^\circ 56'$, n_{D20° 1.49922, acid v. 0.3, ester v. about 63.5 (the change of colour when titrating was rather indistinct), ester v. after acetylation 70.3, soluble in 5.5 vols. and more of alcohol of 90 per cent.

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[1]) *Perfum. Record* 12 (1921), 51. — [2]) *Perfum. Record* 12 (1921), 90. — [3]) *Zur Kenntnis des Curcumaöls* I. Helsingfors 1921. — [4]) Comp. *Report* April 1911, 57.

The herb without roots, but flowering more abundantly, yielded about the same quantity of oil (0.26 per cent.). It was a little heavier and seemed to be strongly predisposed for resinification: d_{15° 0.8836, $\alpha_D + 50^\circ 4'$, n_{D20° 1.50624, acid v. 0.3, ester v. about 70.9 (see above), ester v. after acet. about 81.9, soluble in 4 vols. and more of 90 per cent. alcohol with slight turbidity.

Both oils were brownish yellow and smelled feebly aromatic. When diluted their odour somewhat resembled that of neroly. No similarity with caraway, however, noticed with oils previously distilled[1]), could be stated.

Essential Oils, Sicilian and Calabrian.

The exports from the chief shipping place Messina in 1921 presented the following aspect: —

Destination	Lemon oil Kilos net	Bergamot oil Kilos net	Orange oil Kilos net	Mandarin oil Kilos net	Other Citrus oils Kilos net
Argentina	3197	776	97	—	60
Austria	188	116	50	—	—
Belgium	1119	396	293	—	—
Canada	3517	246	—	—	—
Denmark	2264	540	509	—	—
Egypt	675	—	10	—	—
Australia	20271	407	146	—	—
France	15465	6830	3335	202	32
Germany	28571	9078	8629	71	—
Japan	462	1516	—	—	48
Great Britain	110714	10460	14174	441	60
British India	658	130	106	—	—
Dutch Indies	100	100	—	—	—
Norway	600	—	—	—	—
Holland	6485	2125	4188	—	—
Rumania	—	77	50	58	—
U. S. A.	239317	16364	31049	—	—
Sweden	645	545	285	—	—
Spain	2728	810	158	—	—
Switzerland	211	—	—	—	—
Uruguay	455	130	90	—	—
Czecho-Slovakia	524	100	278	—	—
Turkey	—	112	—	—	—
Bulgaria	25	—	—	—	—
Portugal	120	—	—	—	—
British South Africa	300	—	—	—	—
Greece	210	22	53	—	10
Total kilos net	438821	50880	63500	772	210

Altogether kilos net 554183.—
against „ „ 569744.— in 1920.

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[1]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 604.

These exports were distributed over the various months as specified hereafter: —

		1920	1921
January	kos gross	98851.—	66865.—
February	„ „	81735.—	173851.—
March	„ „	102096.—	105497.—
April	„ „	67280.—	108987.—
May	„ „	50533.—	70009.—
June	„ „	53348.—	85988.—
July	„ „	53102.—	48397.—
August	„ „	41332.—	27310.—
September	„ „	45015.—	49214.—
October	„ „	76721.—	51198.—
November	„ „	142904.—	44691.—
December	„ „	133133.—	72868.—
	kos gross	946050.—[1]	904875.—[1]

Average prices in 1921.

The prices are understood in Italian Lire for 1 Sicilian pound of 317 grams.

Month	Lemon oil	Bergamot oil	Orange oil, sweet	Orange oil, bitter	Mandarin oil
January: 3rd to 8th	11.75	82.—	46.—	35.—	100.—
„ 10th „ 15th	11.75	81.—	46.—	34.—	95.—
„ 17th „ 22nd	11.—	80.—	45.—	32.—	95.—
„ 24th „ 31st	10.—	79.—	44.—	31.—	93.—
February: 1st „ 5th	9.50	77.—	43.—	32.—	90.—
„ 7th „ 12th	9.50	77.—	43.—	32.—	85.—
„ 14th „ 19th	9.50	77.—	43.—	32.—	85.—
„ 21st „ 26th	9.25	75.—	42.50	31.—	83.—
March: 1st „ 5th	8.50	73.—	41.—	30.—	80.—
„ 7th „ 12th	8.50	72.—	40.—	28.—	78.—
„ 14th „ 19th	8.50	70.—	40.—	28.—	78.—
„ 21st „ 31st	8.25	69.—	40.—	28.—	78.—
April: 2nd „ 9th	7.—	66.50	34.—	24.—	70.—
„ 11th „ 16th	6.50	68.—	34.—	23.—	67.—
„ 18th „ 23rd	6.—	68.—	33.—	23.—	55.—
„ 25th „ 30th	5.75	66.—	33.—	23.—	55.—
May: 2nd „ 7th	5.50	64.—	31.50	22.—	50.—
„ 9th „ 14th	5.25	62.—	31.—	22.—	50.—
„ 16th „ 21st	5.25	60.—	30.—	21.—	45.—
„ 23rd „ 31st	5.50	58.—	28.—	20.—	45.—
June: 1st „ 4th	5.80	50.—	23.—	17.—	40.—
„ 6th „ 11th	5.80	50.—	20.—	17.—	45.—
„ 13th „ 18th	6.—	54.—	—	—	45.—
„ 18th „ 30th	7.—	55.—	—	26.—	50.—

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[1]) The net weight is arrived at by deducting 40 per cent.

Month	Lemon oil	Bergamot oil	Orange oil, sweet	Orange oil, bitter	Mandarin oil
July: 1st „ 9th	7.75	55.—	34.—	26.—	50.—
» 11th „ 16th	7.75	53.—	32.—	26.—	50.—
» 18th „ 23rd	7.25	53.—	31.—	27.—	59.—
» 25th „ 30th	7.75	55.50	35.—	28.—	62.—
August: 1st „ 6th	8.50 to 11.—	60.— to 68.—	38.50	30.—	65.—
» 8th „ 13th	10.50	78.—	43.—	32.—	70.—
» 16th „ 20th	9.75 to 11.—	78.—	47.—	33.—	75.—
» 22nd „ 30th	10.—	74.—	47.—	49.—	85.—
September: 1st „ 10th	9.75	73.50	46.—	48.—	83.—
» 12th „ 17th	9.25	72.—	45.—	46.—	83.—
» 19th „ 24th	8.80	71.—	43.—	48.—	83.—
» 26th „ 30th	8.75	70.50	41.25	50.—	78.—
October: 1st „ 8th	8.50	70.—	40.—	45.—	76.—
» 10th „ 15th	8.30	78.—	39.—	41.—	74.—
» 17th „ 22nd	7.75	70.—	38.—	37.—	75 —
» 24th „ 29th	7.50	70.—	39.—	34.—	72.—
November: 2nd „ 5th	8.—	70.—	42.—	33.—	71.—
» 7th „ 12th	8.—	68.—	43.—	34.—	70.—
» 14th „ 19th	7.75	67.—	41.—	34.—	70.—
» 21st „ 26th	7.50	63.—	40.—	34.—	65.—
» 28th „ 30th	7.—	61.50	39.—	33.50	65.—
December: 1st „ 3rd	7.—	61.—	38.—	33.50	60.—
» 5th „ 10th	7.—	60.50	38.—	34.—	60.—
» 12th „ 17th	7.50	60.—	38.—	34.—	55.—
» 19th „ 24th	8.—	59.75	37.50	32.—	55.—
» 26th „ 31st	8.50	60.—	37.—	31.—	55.—

Bergamot Oil. — After a short period of comparative firmness towards the end of April last year, the market relapsed into the old dull state, so that the prices sank nearly 20 per cent. Attempts made from certain quarters to monopolize the market, failed. Only in the course of the month of August, a sudden change took place, owing to a vivid demand from all foreign countries, which coincided with the purchases speculators had to make in order to cover their engagements. However, there was a noticeable downward tendency again already in the following two months, as the coming new crop induced various producers to put their stocks on the market. The yield of last year's autumn pressing is somewhat lower than the previous one, but in consequence of lack of transactions the position of the article continues weak. One may therefore reckon with further declining prices.

A. Parozzani¹) investigated bergamot oils of the 1921/22 Calabrian crop. Whereas the oils of the previous year were conspicuous by their high optical rotation, low

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¹) *Annali della R. Stazione Sperimentale per l'industria delle essenze e dei derivati dagli agrumi* 2 (1922), 1. According to a reprint kindly sent us.

ester content and defective solubility, most of the products now dealt with showed almost normal constants: The specific gravity is generally in proportion with the ester content (there are no exact indications), $\alpha + 12$ to $+ 22°$ (on an average $+ 16$ to $+ 17°$), soluble in 80 and 82.5 per cent. alcohol, ester content 31 to 36 per cent. for the oil prepared in November/December and 36 to 39 per cent. for that obtained in January/February. In some regions, the optical rotation of the oils was $\alpha + 28$ to 31°.

It results from these constants, as the author remarks, that the effects of the drought in summer 1920 is less noticeable in the quality of this year's product than in that of last year's crop, but there is not a similar improvement in the yield. The quantity expected is only 70 to 75000 kilos, *i. e.* less than half a normal crop.

With regard to the remarks which we connected with our discussion of Parrozani's publication on bergamot oil of the 1920/21 crop (our last *Bericht,* p. 20), the author points out that the constants established by him do not refer to the oils from fallings but to those of ripe fruits. He further states that the samples have always been collected by officials of the stations in the various producing districts, who also watched the manufacturing process. The high rotatory power of the oils (α up to $+ 37°$) was easily explained by that of the terpenes contained therein (α up to $+ 72°$). There could not be any suspicion of adulteration with lemon or orange oils. Besides, his figures were not intended to be a firm criterion for bergamot oils, but meant to show that absolutely pure oils may sometimes have abnormal constants.

Lemon Oil.—The downward tendency, of which we reported a year ago, lasted until May, when such a low price level was reached that all concerned in the lemon oil trade had to sustain the most serious losses. A fairly brisk demand which then arose, sent the prices up a little, but only for a very short time, as the rumours of bad prospects for the next crop proved to be exaggerated. Even a vivid demand, especially from the United States, in the course of September, only led to a very moderate hardening of the market, and although the October shipments were twice as large as those of the previous month, no considerable rise was caused, as the imminent new crop induced the producers to come forth with their stocks. The yield was normal and taking into consideration the quantities still available of the old crop, it is thought that a further decline of the prices may be predicted, as speculative attempts to bring about a change have always only had a temporary effect. Only if the chief places of consumption showed a much keener interest in the article, conditions might alter.

Sicily supplies 88 per cent. of the total Italian lemon crop, whereas Calabria only contributes 4, Campania 3.5, Apulia and Liguria 2 each and Sardinia 0.5 per cent.[1]). Most of the fruits are exported, only part being used for the manufacture of the essential oil. In Palermo 90 per cent., in Siracusa 60 per cent. and in Catania 40 per cent. of all the Citrus trees grown are lemon trees. The varieties cultivated most are those producing oval fruits with a thin and smooth skin. Good lemons are supposed to have pale yellow skin without any excrescences, sour juice and few pippins. In Sicily, the following classification is made according to the time of gathering:— A) *Marzioli* or *Massani.* They ripen in December, provided that favourable weather immediately after the normal crop, *i. e.* in March, produces another bloom. B) Lemons. They are the fruits of the normal bloom in April and May, ripening from December to February and being collected during these months. C) *Biancucci* or *Bianchetti,* also

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[1]) H. C. Holtz, *Chem. Weekblad* 18 (1921), 108.

called *Ricioppi*. These ripen after the normal crop and come from June blossoms. D) *Verdelli*. They are summer fruits, forced to premature ripening by a special process. The trees are left dry until the end of July, but then watered profusely. This causes an abundant bloom in August and September, so that the still greenish fruits can already be gathered in the following summer. Although this proceeding shortens the life of the trees from 80 to 40 or 50 years, the yield of *Verdelli* offers ample compensation for this disadvantage. E) *Bastardi* or *Bastardoni*. These are the names of the belated fruits of the *Verdelli* crop, gathered in August. It is said that the rotatory power of the oil from *Bastardoni* and *Bianchetti* is not higher than 54°[1]).

For the manufacture of the essential oil, only such lemons are used, the abnormal size or form or other undesirable qualities of which make them unfit for being exported. These rejected fruits amount to about 25 per cent. in the Palermo and Siracusa districts, whereas in those of Messina and Catania they may come up sometimes to 75 or even 80 per cent. of the crop.

According to De Salvo, 63000 lemons yield 100 Sicilian pounds = 32 kilos of oil. The same as with the bergamots, more and better oil is obtained from green than from ripe fruits. In consequence, the lemons gathered from December to February are to be preferred. The lemons growing near the coast of Amalfi (Campania), for instance, which ripen very late (in summer), contain so little oil that is does not pay to obtain it.

Messina is the most important Sicilian export harbour for lemon oil, although a certain part goes from Catania and Siracusa. Reggio is the centre for the oils produced in Calabria.

Of the various methods of determining the citral content, Holtz considers to be the best those of Walter and Bennett (with hydroxylamine)[2]), Kleber (with phenylhydrazine) and Romeo (with neutral and acid sodium sulphite). The last-named method, by means of which according to Berté and Patané[3]) a citral content of 4 to 5.6 per cent. is found for good lemon oils, is used in the laboratory of the Messina Chamber of Commerce. Patané thinks[4]) that far too much value is attached in commerce to the citral content, which ought not to be less than 4 per cent.[5]). The aroma of the oil depends on other constituents, present in small quantities and which do not come into consideration for the usual chemical analysis. The lemon oils of the finest aroma, *i. e.* those of the November/December crop, contain less citral than the inferior qualities of February/March.

Orange Oil, bitter.—The lowest price level was reached towards the middle of June, with 17 Lire, until in the middle of July the general rise of all the citrus oils also affected this article. The climax was 50 Lire, end of September, but already in October the price had gone down again to 34 Lire. The new crop is satisfactory, and as there are old stocks from 1920 one may reckon with a continued feeble tendency for the next months.

Orange Oil, sweet.—The price, which in March 1921 was still 40 Lire, sank to one half of it towards the middle of June, hardened gradually during the months of July and August, reaching its highest stage end of the latter month at about 47 Lire.

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[1]) According to other observations, +54° is the lowest limit, down to which the optical rotation may go. Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. III, p. 17. — [2]) In our opinion this method is to be preferred, although the figures arrived at are 10 per cent. too low, referred to the amount of citral present. Comp. *Report* October 1909, 154. — [3]) *Riv. Ital. Essenze e Prof.* 1919, I., p. 7 and 30. — [4]) *Id.* p. 7. — [5]) Comp. *Report* April 1914, 58.

This rise was chiefly due to the vivid demand from abroad, but it was accentuated by the supposition that the lasting rain would seriously damage the blossom. Besides, speculative purchases were made to a very great extent, with a view to force the article into an upward movement. This scheme did not succeed, however, owing to the buyers' refusal to pay the high prices demanded and to the approaching new crop. A firmer tendency, noticed in March, was only temporary, and at present the article is rather neglected, the same as the other Citrus oils.

According to official statistics[1], the Italian orange crop originated as follows:— Sicily 57 per cent., Calabria 20 per cent., Campania 16 per cent., Apulia 3 per cent., Liguria 0.7 per cent., other districts 3.3 per cent. Only second-rate fruits are used for manufacturing the oil, 70 000 oranges being required for producing 100 Sicilian pounds, equal to about 70 English pounds. According to the statistics of the Exchequer, the exports of bitter and sweet orange oils were as follows:—

1917	72 347	k^{os} to the value of	2 532 145	Lire
1918	49 109	„ „ „ „ „	1 964 360	„
1919	103 913	„ „ „ „ „	4 156 520	„

France, the United States and England were the principal importers.

In 1919, Jamaica exported 168 415 lbs. of orange oil. According to an English periodical[2], this large shipment was due to the exceptionally good price obtainable for the oil. Jamaica's capacity for orange production is nearly a million boxes at present. Within ten years this output might be doubled, if she could obtain a regular profitable market. But the prohibitive U. S. A. tariff against Jamaican fruit and restricted shipping to the United Kingdom held back orange cultivation. The Jamaica Agricultural Society is urging the Government of the Island to make further representations to the Canadian Government for a preferential duty on West Indian fruit. This the Canadian Government have so far declined to do, alleging that the British West Indies can only supply a small portion of the amount required. Jamaica replies that, given such encouragement, there would at once be a responsive effort in making her neglected trees more productive, and new plantations would be engaged in, for certain districts in the island have such conditions as make orange cultivation their best industry.

P. Mirgodin[3] describes a so-called "new" machine, constructed by the "Ecuelles Ltd." and invented by two West Indian planters, with the aid of which the essential oil can be obtained from the various citrus fruits. He states that from 0.5 to 1 oz. of lemon oil and 2 to 3 ozs. of orange oil or oil of limes can be got from one bushel of fruits. The machine is constructed in three different sizes. It results from Mirgodin's description that the peeling process, described years ago by Hood and discussed by us[4] is here referred to.

A disease which occurs in most citrus-growing countries and is fairly prevalent in Australia, the so-called collar rot[5], often escapes the notice of the growers until serious damage has been done. Its appearance and treatment are described in Agric. Gaz., New South Wales (**1920**, 31, 439). Collar rot manifests itself most frequently by "gumming" on the trunk just above or close to the ground. In many cases the bark in the vicinity is dry and brittle. In young trees the leaves show "yellowing", or chlorosis, especially on terminal twigs, but in older trees chlorosis may not develop

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[1] H. C. Holtz, *Chem. Weekblad* 18 (1921), 108. — [2] *Perfum. Record* 12 (1921), 184. — [3] *Parfum. moderne* 14 (1921), 257. — [4] Comp. *Bericht* (German) 1920, 32. — [5] *Bull. Imp. Inst.* 18 (1920), 437.

until the attack has reached an advanced stage, when the tree has been nearly ring-barked. Associated with the disease[1]), a fungus parasite *(Fusarium limonis)* is constantly found, which enters the tree at an injured part, goes very slowly through the tissues of the trunk, and if left unchecked accomplishes the ring-barking of the tree. The treatment recommended when "gumming" has been observed is to scrape the earth away from the base of the tree, remove the dried bark apparently infected by the fungus, and paint the wound with a bluestone paste composed of $1^1/_2$ lbs. of copper sulphate, 4 lbs. of unslaked lime and $1^1/_2$ gallons of water. Where collar rot is too far advanced for the tree to be saved by this treatment it should be removed and burned, and the stump-hole limed. Bad drainage is conducive to this disease.

Estragon Root Oil.—Estragon roots, collected in Miltitz, yielded on distillation with steam 0.21 per cent. of a dark brown oil. The feeble smell recalled somewhat that of radishes and was, in any case, entirely different from that of the herb:— d_{15° 0.9744, n_{D20° 1.56406, acid v. 2.1, ester v. 14.4, soluble in 5 vol^s of 90 per cent. alcohol with turbidity, which gradually diminishes on further dilution. Owing to the dark colour, it was impossible to determine the optical rotation.

Eucalyptus Oil.—As per an American report[2]), the eucalyptus oil industry in Victoria appears to be in a very low condition, many of the distillers having ceased to work. In the Maryborough district, only one distillery is at work. In the Neilborough district, about half the factories are working, but only at low-grade oils.

In a communication dealing with piperitone, J. Read and H. G. Smith[3]) furnish some details concerning the history of the "peppermint" eucalypts of Australia.

Soon after the arrival of Governor Phillip in New South Wales, in 1788, a species of this peppermint type, growing plentifully in the neighbourhood of Port Jackson attracted the attention of the colonists, and the first eucalyptus oil to be distilled was obtained from its foliage and employed for medicinal purposes by Surgeon-General Dr. White, who gave the plant the name Peppermint Tree on account of the very great resemblance between the essential oil drawn from its leaves and that obtained from the peppermint in England. The oil was found by Dr. White to be much more efficacious in removing all cholicky complaints than the English peppermint oil. Nowadays, the tree is known to have been *Eucalyptus piperita,* which is common in the Sydney district and the Blue Mountain Ranges of New South Wales[4]).

The eucalypts of the "peppermint" group are now known[5]) to contain piperitone $C_{10}H_{16}O$ (*p*-menthenone-3), occurring, with the exception of *E. apiculata,* in association with l,α-phellandrene and, in most cases, also with the corresponding secondary alcohol piperitol. When isolated in the usual way, by fractional distillation under atmospheric pressure followed by treatment with sodium hydrogen sulphite solution, the piperitone, on regeneration, undergoes racemisation and usually exhibits a feeble lævoratation not exceeding $[\alpha]-1^\circ$. Read and Smith ascribe this to the possible presence of small quantities of the lævorotatory aldehyde "cryptal". By conducting the distillations,

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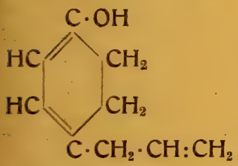
[1]) According to the description the so-called "gumming" disease *(gummosis),* which may attack all sorts of citrus-trees, seems to be referred to. Comp. *Bericht* (German) **1921**, 89. — [2]) *Americ. Perfum.* **16** (1922), 318. — [3]) *Journ. chem. Soc.* **117** (1921), 779. — [4]) Comp. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd edition, vol. III, p. 277. — [5]) *Ibidem,* p. 283.

however, under greatly diminished pressure it is possible to isolate the piperitone in its natural, markedly lævorotatory form ($[\alpha]_D$ −42.8°)[1]).

A specimen of piperitone obtained by Read and Smith from the essential oil of *Eucalyptus dives* by distillation under atmospheric pressure and by purification by means of neutral sodium sulphite, showed the constants: — b. p. 128.5° (25 mm.), $[\alpha]_D$ −0.27°, $n_{D20°}$ 1.4843; hydroxylamino-oxime, m. p. 169 to 170°; oxime, m. p. 110 to 111°; semicarbazone, m. p. 219 to 220°. (The semicarbazone prepared by Wallach[2]) from Δ^1-*p*-menthenone-3 had the m. p. 224 to 226°.) On treating piperitone with benzaldehyde in presence of metallic sodium the authors obtained benzylidene-*d,l*-piperitone $C_{10}H_{14}O:CH\cdot C_6H_5$, m. p. 61°; oxime, m. p. 130 to 131°.

The bimolecular ketone $C_{20}H_{34}O_2$ from piperitone obtained by Baker and Smith, under the identical conditions, yielded no benzylidene compound.

From the oil of *Eucalyptus hemiphloia,* R. T. Baker and H. G. Smith[3]) succeeded in obtaining a new crystallised phenol which they termed *australol.* This phenol, which occurs also in other oils of the "Boxes", was prepared in the same manner as tasmanol (comp. *Report* **1916**, 30) and showed the following constants: — m. p. 62°, b. p. 115 to 116° (10 mm.), $d_{20°}$ 0.9971, $\alpha_D \pm 0$, $n_{D20°}$ 1.5195, mol. refr. found 41.50; calculated for three double bonds 41.74; benzoate, m. p. 72 to 73°. In alcoholic solution, ferric chloride gave with the phenol a fleeting greenish yellow colour at first, quickly changing to bright yellow. The odour of australol reminded of ordinary phenol, and the skin was attacked by the new phenol in exactly the same manner as by phenol. Combustion and molecular weight determination proved the empirical formula $C_9H_{12}O$. Since the unsaturated phenol gave no colour reaction with picric acid, the unsaturated side-chain has most probably the allyl grouping, two double bonds thus occurring in the nucleus. The authors conclude, therefore, that australol is a dihydro-*p*-allylphenol of the structure given above.



Probable structure of australol.

From the oil of *Eucalyptus hemiphloia* and related eucalypts, Baker and Smith obtained formerly[4]) an aldehydic body which they termed aromadendral. Recently[5]) it was found that this body, which occurs likewise in the oils of the "Box" and "Mallee" group, was no uniform substance, but a mixture of aromadendral proper, $C_{10}H_{14}O$, with cuminal $C_{10}H_{12}O$, phellandral $C_{10}H_{16}O$ and a new aldehyde "cryptal" $C_{10}H_{16}O$. The latter aldehyde had escaped the authors in their first investigation, because it did not form a solid compound with sodium bisulphite, and the liquid combination is not decomposed by sodium carbonate. These very properties afforded later on a satisfactory method for the preparation of the new aldehyde. According to a method given in detail, the authors succeeded in isolating, as they believe, pure cryptal from the oils of *Eucalyptus hemiphloia* and *E. polybractea.* However, the constants of both aldehydes do not agree with each other[6]).

Cryptal from the oil of *E. hemiphloia:* — b. p. 99 to 100° (10 mm.), 221° (760 mm.), $d_{20°}$ 0.9431, α_D −76.02°, $n_{D20°}$ 1.4830; semicarbazone m. p. 176 to 177°; oxime and hydrazone were liquid.

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[1]) Comp. *Bericht* **1921**, 24. — [2]) *Liebig's Annalen* **362** (1908), 272. — [3]) Baker and Smith, *A Research on the Eucalypts and Their Essential Oils*, 2nd edition 1920, p. 396. — [4]) Comp. *Reports* April 1901, 34; October 1901, 29. — [5]) Baker and Smith, *A Research on the Eucalypts and Their Essential Oils*, 2nd edition, 1920, p. 383. — [6]) No explanation is given for this discrepancy.

Cryptal from the oil of *E. polybractea*: — d_{20° 0.9443, α_D — 49.7°, n_{D20° 1.4849; semicarbazone, m. p. 180°; oxime and hydrazone were liquid.

Attempts to separate aromadendral $C_{10}H_{14}O$ from the other aldehydes present in the oil in the pure state, were hitherto without success, cuminal being mostly present.

Oil of the Bark of Eucalyptus Macarthuri. — From the ground bark of *E. Macarthuri*, Deane et Maiden, a species cultivated on a large scale near Emerald, Victoria, Baker and Smith¹) obtained by steam-distillation 0.12 per cent. oil of a light amber colour and a distinct odour of geranyl acetate. Three different samples of this oil showed the following constants: — d_{15° 0.9099 to 0.9218, α_D + 1.2 to + 1.4°, n_{D20° 1.4648 to 1.4718, soluble in 1.2 vols. of 70 per cent. alcohol, ester v. 169.5 to 195, equal to 59.2 to 68.2 per cent. geranyl acetate; ester v. after acet. 198.8 to 224, equal to 69.6 to 78.4 per cent. ester.

The optical rotation of the oil is ascribed to the presence of a small quantity of *d*-pinene. Eudesmol, a constant constituent of the leaf oil from *Eucalyptus Macarthuri*, dœs not appear to be present in the bark oil. Apart from this, the constants of both oils appear to be fairly identical.

Fennel Oil. — Our industry has not seen much of the good yield of last fennel crop, as the largest share by far was sent abroad, where higher prices were obtainable. Even the factories situated in the vicinity of Lützen fennel districts did not succeed in buying fair quantities. It would have been better if the Government had taken the suggested measures for stopping the export, or at least restrict it, so that the work connected with the distillation of the fennel seeds remained in the country. It is to be hoped that something will be done with regard to the next crop, as otherwise the distillation of fennel oil will pass entirely out of the hands of the German industry.

C. E. Sage²) examined two fennel oils of Spanish origin and known to have been prepared from the entire plant of *Fœniculum vulgare*. The following constants, found by him, seem to indicate that the products in question were at least partly composed of bitter fennel oil: — $d_{15.5^\circ}$ 0.9203, and 0.9340, α_D + 46° and + 24°, n_{D25° 1.4945 and 1.4980, soluble in 1 vol. of 90 per cent. alcohol, congealing point . . . no indication at — 15°.

Frankincense Oil. — By fractionated distillation of 1 kilo of terpeneless oil of frankincense³) in a vacuum, E. Fromm and R. Klein⁴) obtained a body $C_{10}H_{16}O$, b. p. 117 to 119° (22 mm.), 210 to 211° (ordinary pressure), d_{18° 0.9504. This compound, called *α*-olibanol by the authors, was not identical with the olibanol prepared by Fromm and Autin⁵), also from oil of frankincense, as it did not yield any pinonic acid on oxidation with potassium permanganate. The olibanol that yielded pinonic acid could be obtained, however, if the oil of frankincense or the product of the distillation were distilled under ordinary pressure. There are in consequence two olibanols; *viz.*, *α*-olibanol, as found in the natural oil of frankincense, and *β*-olibanol, formed through a re-arrangement of the molecules on heating the former above its boiling point. As *α*-olibanol does not yield any pinonic acid, it is neither identical with verbenol, nor with dihydroverbenone. On reducing *α*-olibanol with sodium and alcohol, dihydro-olibanol is formed, $C_{10}H_{18}O$ (b. p. 100 to 102° [25 mm.], *o*-nitrobenzoate, m. p. 135 to 137°), which is not identical with dihydro-verbenol.

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¹) *A Research on the Eucalypts and Their Essential Oils*, 2nd edition **1920**, p. 318. — ²) *Perfum. Record* **12** (1921), 46. — ³) Cf. page 142 of this *Report*. — ⁴) *Liebigs Annalen* **425** (1921), 213. — ⁵) Cf. *Report* April **1914**, 63.

When trying to reduce the β-olibanol in the same way, the authors only obtained the unaltered material, in addition to resinous products.

An ordinary oil of frankincense, distilled *in vacuo*, yielded a compound $C_{10}H_{16}O$ (b. p. 114 to 116° [15 mm.], d_{15° 0.9502). This product (γ-olibanol) which it was impossible to reduce like α-olibanol or to transform into the β-compound by heating, yielded on oxidation a liquid acid and did not react with semicarbazide. Even after ordinary oil of frankincense had been stored for five years, no α-olibanol had formed in it.

Geranium Oil. — The production of geranium oil in North Africa has decreased considerably. Whereas 140000 kilos were distilled in Morocco, Algiers and Tunis, in 1914, only 15000 kilos were obtained in these three countries in 1920. In consequence, the price rose from 30 or 35 Francs in 1914 to 250 Francs per kilo in 1920. There was a change, however, in 1921, for in spite of a very small crop (only 14000 kilos) not more than 70 Francs were paid per kilo in the producing districts. As the geranium growers find these low prices unprofitable, they intend giving up the cultivation of the geranium plant altogether[1]).

A. Rolet[2]) reports on the crops and the yield of geranium plants in various countries, where the plant is cultivated. The time of the crop varies according to the district and the way of cultivating. In the Provence, the crop takes place in August/September, very rarely for a second time in October/November. As the plants would freeze in winter, a fresh cultivation must be started every year. As soon as the leaves lose their lustre, the plants are mown, preferably towards evening on fine days, so that the herb does not dry out too much.

In Corsica (*Pelargonium odoratissimum*), there are two cuts, in May and August, very seldom a third one in September/October, when only slips come into consideration[3]).

In Algiers, the crop begins already in spring, generally in April, as soon as the plants start flowering. There is a second cut in June/July and a third one in October-November. There are five crops within two years, the yield being smaller in the first year than later on. On good soil, such as in Boufarik, the stalks are from 50 to 70 cm. long, otherwise they only measure from 25 to 30 cm.[4])

In Italy (*Pelargonium roseum*, Willd.), there is only one crop in the first year of cultivation, in August/September, whereas in the second year the plants are cut in May, August and October/November. The plants can be used there for four, sometimes even for up to eight years. If only the flowers are gathered, the oil of which is supposed to be finer, according to Blandini[5]), the crops are more frequent. The author once started on the 18th of April in Portici and left off gathering the flowers on June 14th, after having had eight crops.

In Réunion, one crop follows the other[6]). If the intention is to keep up the cultivation for several years, the plants are cut down more than if they are renewed every year. In order not to uproot the plants, tree-shears are used for cutting in the first year and sickles later on. The cut plants are sent at once to be distilled, for if they stay in heaps for some time they get hot, start fermenting and lose in value.

The output varies and depends on all sorts of circumstances, such as way of cultivating, soil, manure, irrigation, number of crops, &c.

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[1]) *Zeitschr. d. Deutsch. Öl- u. Fett-Ind.* **41** (1921), 825. — [2]) *Parfum. moderne* **13** (1920), 60. — [3]) Comp. *Report* October **1910**, 70. — [4]) Comp. *Report* October **1913**, 61. — [5]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2ed edition, vol. II, p. 614, foot-note 5. *Report* April **1907**, 54. — [6]) Comp. *Report* April **1914**, 64.

In the Alpes Maritimes in France, from 25 to 80000 kilos (on an average 40000 kilos) per hectare and year can be obtained on well irrigated, artificially manured soil, if great care is taken of the plants. In the Var department, the yield may come up to 75 and even 100000 kilos per hectare, according to L. Robertet.

In Algeria the crops are estimated at from 25 to 27000 kilos per hectare.

Blandini obtained from *Pelargonium roseum,* Willd., in Italy 26000 kilos of herb and 3945 kilos of flowers per hectare.

R. Knuth[1]) has published an extensive article on geranium oil (botany, distribution, cultivation and yield of the mother-plant and its varieties, chemistry of the oil and its components), with several good pictures of *Pelargonium* species. The author thinks that the plants cultivated in the various countries may be considered either as varieties of cultivation or hybrids of other species, whose origin is now unknown or has been forgotten long since. In the beginning of the nineteenth century, there was a sort of fad to hybridize *Pelargonium* species, so that, for instance, the *Geraniaceæ* of Sweet[2]) (London 1820—1830) contain almost 500 of such artificial hybrids, whose origin already at that time had been partly unknown. In the course of time, the origin of each cross became more and more obscure, so that at the present time we are unable to determine te exact origin of a large part of the pelargoniums found in our botanical gardens. This is especially the case with regard to the species which were called lemon-geraniums as early as the time of Sweet, and with which the rose-geranium must be included[3]).

Andrews[4]), in his *Geraniums* (1805), mentions a *Pelargonium oxoniense*[5]), closely related to *Pelargonium graveolens* and *Pelargonium capitatum,* which was first cultivated in Oxford on account of its rose-odour and sold under the name of *Oxoniense roseum.* Knuth thinks it very probable that the parent plant of the rose-geranium was originally purchased under the name of *Oxoniense roseum* and is related to *Pelargonium oxoniense.* Heuzé[6]) and Cordemoy[7]) are mistaken in thinking that the species chiefly cultivated in Algeria and Réunion is *Pelargonium capitatum,* as the plant found there has leaves entirely different in shape from those of *P. capitatum.* This species rather belongs to the group of *Pelargonium graveolens,* L'Hérit.

It is probable that in France, in addition to rose-geranium, *Pelargonium odoratissimum* (L.), Ait. (belonging to the section of *Peristera,* according to Harvey) and *Pelargonium fragrans,* Willd. (a hybrid of *Pelargonium odoratissimum* and *P. exstipulatum,* L'Hérit.) are cultivated, though to a smaller extent. Both plants have a delicate texture and differ also in other ways from the rose-pelargonium. In Algeria and Réunion the two species are certainly not cultivated.

The oil is furnished by the glands of the plant. These are found, as in all pelargonium species, in the green parts, especially on the surface of the leaves, where they are shorter than on the stem and the peduncles. In most cases they are from $^1/_{18}$ to $^1/_{15}$ mm. long and can be seen with the naked eye. They consist of from one to three small cylindrical base cells and a small globular head, in which latter the oil is generally to be found When young, the end cell is colourless, later on it is coloured by a yellow substance and finally becomes brown. The oil glands are of great use to the plant, as they protect it against insects and snails. As a matter of fact, all pelargoniums are but little damaged by such enemies.

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[1]) *Americ. Journ. Pharm.* 93 (1921), 302. — [2]) Died as a market-gardener in London. — [3]) Knuth calls "rose-geranium" the chief parent plant of geranium oil. See lower down. — [4]) Herbalist in London, who published precious copper plates of foreign plants. — [5]) *Pelargonium oxoniense,* van Eeden *(Index Kewensis).* — [6]) *Revue Horticole* 65 (1893), 305. — [7]) *Revue Cult. Colon.* 1904, 170.

Blandini's assertion[1] that the *flowers* produce a larger quantity of oil of excellent quality is in Knuth's opinion certainly not in accordance with the facts.

As to the geographical distribution of the plant, the author gives the following summary, many facts of which will be known already from our previous *Reports.* In France the plant was first cultivated near Grasse and at the foot of the Maritime Alps, near Cannes. Though it was known there as early as 1819, it seems to have been grown only to a limited extent up to 1847. Shortly after that time, emigrants transmitted the cultivation to Algeria, where the plant was first grown in the district of Sahel, Western Algeria, between Oran and Mostaganem, afterwards in the plain of Metidja, near Algiers, and in the littoral of the province of Constantine, near Philippeville and Bougie. The cultivation did not spread to Réunion before 1880. It was favoured there by the sugar crisis of 1904—1906. — In the Spanish province of Granada, experiments regarding the cultivation of the plant were made about 1890. Although the quality of the oil was excellent, the area of cultivation, producing from 600 to 1000 kilos annually, was not increased. — In the Jewish colonies of Asia Minor, Rischon-le-Zion and Petach-Tikway, there are plantations which were founded by Baron Rothschild. — The trial plantations of *Pelargonium radula* in Limaru, British East Africa, have not been continued. — The author states that he has not been able to obtain information concerning the cultivation of the plant in Corsica. We would mention that it was introduced there from the Provence, about 1860, and quickly spread in the districts of Erbalunga, Sisco and Brando.

We have reported repeatedly on adulterations of geranium oil with citronella oil or fractions thereof[2]). It is often difficult to recognize such admixtures, as the constants are not always influenced sufficiently to become abnormal. Under these circumstances, a careful examination of the smell will rouse suspicion, but only an exact chemical analysis can give absolute certainly.

We had to deal with such a case quite recently, when a geranium oil was sent us for inspection from Spain. It behaved as follows: — d_{15° 0.9002, $\alpha_D - 6^\circ 38'$, n_{D20° 1.47171, acid v. 5.2, ester v. 50.8 = 21.4 per cent. ester, calculated as geranyl tiglinate, ester v. after acetylation 213.7 = 70 per cent. total geraniol, soluble in 2.3 vols. and more of 70 per cent. alcohol, dilute solution slightly turbid. As the product was supposed to be a Bourbon oil, it struck us that the constants were abnormal in part, the specific gravity and the index of refraction being too high, the optical rotation too low. The sample therefore resembled rather an African distillate, but was suspicious in any case on account of its odour and defective solubility. It was proved through investigation that the oil contained an appreciable quantity of citronellal, a substance which is not a component of geranium oil. With the aid of bisulphite, several grams of citronellal were isolated out of 125 grams of the oil under examination and identified by means of the semicarbazone, melting between 82 and 83°. A mixture with a semicarbazone prepared for the sake of comparison showed the same melting point, so that the identity of the two compounds is certain.

In order to make quite sure, we treated 125 grams each of genuine pure Bourbon and African geranium oils in the same way with sodium bisulphite, when the quantities of aldehydic components obtained were so small that a chemical identification resulted impossible, whereas the smell seemed to indicate citral or a fatty aldehyde rather than citronellal.

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[1]) *Bull. de l'Off. du Gouv. de l'Algérie* **12** (1906), 277. Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, p. 614, foot-note 5. — [2]) Comp. *Report* **1917**, 19 and *Bericht* (German) **1920**, 36.

On account of this result there can be no doubt that we had to deal with an adulteration. We presume that there was an admixture of citronella oil or a fraction thereof, which would explain the defective solubility.

Gingergrass Oil. — Two samples, described as sofia oil, were forwarded to the Imperial Institute from Dehra Dun in 1916. On investigation[1]), the oils revealed the following constants: — $d_{15^\circ}^{15^\circ}$ 0.910 and 0.907; α_D —15° 48′ and —14° 3′; sol. in 2.1 and 2.0 vols. of 70 per cent. alcohol, no opalescence on dilution to 10 vols.; acid v. 2.3 and 1.5; ester v. 25.7 and 19.8; ester v. after acet. 170.5 and 180.6. The oils showed a slight odeur of citral, the absorption test with sodium hydrogen sulphite, however, manifested nothing abnormal in this respect, since the two oils contained 12 and 11 per cent. of matter soluble in that reagent, whereas of a commercial oil 10 per cent. were absorbed.

A further sample of the same oil originating from the United Provinces of India (1917) had the constants: — $d_{15^\circ}^{15^\circ}$ 0.936; α_D + 42.87°; n_{D20° 1.490; insol. in 70 per cent. alcohol; acid v. 4.5; ester v. 13.5; total alcohols, calculated as geraniol, 42.7 per cent.

Oil of the Berries of Heeria paniculosa. — The berries of this anacardiacea[2]), indigenous in Zululand and known there as *isifeku*, yielded on water-and-steam-distillation 4.47 to 6.07 per cent. essential oil[3]). The oil is located especially in the pericarp and shows no particular odour. It consisted for the greater part of terpenes and had the following constants: — d 0.832, α 3.75°[4]), acid v. 1.6, ester v. 4.2, ester v. after acet. 14.8.

Oil of Houttuynia cordata. — By steam distillation of the herb *Houttuynia cordata*, Thunb., a piperacea known as *Dokudame* in Japan, Y. Shinosaki[5]) obtained 0.0049 per cent. of a light brown essential oil with a strong, somewhat disagreeable odour, and the following characters: — d_{15° 0.8744; $[\alpha]_D$ — 5°; n_{D20° 1.4685; acid v. 16.65; sap. v. 28.40. On treatment with sodium bisulphite, methyl *n*-nonyl ketone (semicarbazone, m. p. 122 to 123°) was isolated. Repeated distillation of the residual oil is yielded a terpene fraction, b. p. 60 to 61° (14 mm.), 167 to 168° (766 mm.), as the principal product; this consisted of an aliphatic terpene (probably myrcene) and a small quantity of a cyclic terpene. The oil also appears to contain a solid acid.

Oil of Juniperus taxifolia. — From the leaves and twigs of *Juniperus taxifolia*, Hook. et Arn. (Japanese *shimamuro*), a coniferous plant indigenous to the Ogasawara Islands, Y. Shinosaki[6]) obtained by distillation 0.24 per cent. of a light green oil. Two specimens of the oil had the following characters: — d_{15° 0.8675 and 0.8701; α_D — ? and — 29°; n_{D20° 1.4702 and 1.4718; acid v. 0.94 and 0.0; sap. v. 11.69 and 10.37; sap. v. after acet. 19.60 and 18.89. The oil contained above 50 per cent. of α-pinene (mainly *l*,α-pinene containing a small quantity of the *d*,*l*-α-isomeride) and possibly a bicyclic terpene, a free alcohol ($C_{10}H_{18}O$), ester, sesquiterpene, and sesquiterpene alcohol.

Oil of Juniperus thurifera. — According to L. Lestra[7]), there is only a difference in the size and the build of the fruits between *Juniperus thurifera*, var. *gallica*, De Coiny, growing wild in France, and *Juniperus thurifera*, L., occuring in Portugal, Spain and

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[1]) *Bull. Imp. Inst.* **18** (1921), 343. — [2]) This species is not mentioned in the *Index Kewensis* of **1910**. — [3]) *Chem. News* **120** (1920), 277. Acc. to *Bull. Roure-Bertrand Fils*, April **1921**, 135. — [4]) The direction of rotation is not quoted in the abstract. — [5]) *Journ. chem. Ind. Japan* **24** (1921), 557. *Journ. Soc. chem. Ind.* **40** (1921), A. 560. — [6]) *Journ. chem. Ind. Japan* **24** (1921), 202. *Journ. Soc. chem. Ind.* **40** (1921), A. 411. — [7]) *Parfum. moderne* **14** (1921), 210.

North Africa. The plant is also easily distinguished from other *Juniperus* species, like the very similar *Juniperus Sabina*, L., especially by the compactness and the shape of the sclerogen cells of the berries. After giving an exact botanical description of *Juniperus thurifera*, var. *gallica*, De Coiny, Lestra reports on the essential oil obtained by steam distillation of the various parts of the fresh plant. The yield amounted to 0.15 per cent. of a straw-coloured viscid oil (0.096 per cent. of the dry plant). The constants were as follows: — d_{15° 0.9115, $\alpha_D + 32.2^\circ$, n_{D20° 1.4963, soluble in chloroform and in 96 per cent. alcohol, in 20 parts of 70 per cent. alcohol, in 10 parts of ligroin (?), acid v. 6.5, sap. v. 67.4, ester v. 60.9 (ester content 21 per cent., in addition to 0.57 per cent. of free alcohol), iodine v. 24.5. Through experiments with animals, it was established that the oil is an emmenagogue, like oil of savin.

Lavender Oil. — When last year's crop began, the market was very weak, for in consequence of the sluggish sales a considerable part of the previous campaign (it is rumored even about half) was still unsold in the South of France. The prices offered to the gatherers were low in consequence, only 20 to 30 Francs per 100 kilos of flowers being paid, according to the district. It is to be taken into account that the usual daily wages amount to 15 or even 17 Francs and that one man cannot gather more than 70 to 80 kilos per day. No wonder that the gatherers restricted their work to the more easily accessible districts, *i. e.*, the lower regions. This may account for the fact that, according to the unanimous judgment of our informants, the ester content of the oils was somewhat lower, on an average, than in the previous year, for the qualities with a high percentage are distilled exclusively of flowers from high regions. Owing to the low collectors' wages, only half the crop, which was very good last year, is said to have been gathered. At first, good lavender oils only fetched from 55 to 60 Francs per kilo and there was very little demand. Only after the annual lavender oil fairs, the most important one of which took place at Digne on October 1st, the market became firmer, as some Grasse firms purchased considerable quantities. Business resulted more brisk early in December, due to a fair demand from abroad, and towards the middle of January about 100 Francs had to be paid for good qualities of 40 per cent. ester. Then there was a pause and the market is quiet now with a slight downward tendency. If nothing unforeseen happens and the demand continues slack, there may be a decline in the next months. However, it will scarcely be considerable, as a good many owners mean to keep back their production, being convinced that the rising costs of gathering, distilling, etc., will influence the coming crop and send prices up. Besides, there is the possibility of smaller crop this time.

According to a *Bulletin du Syndicat des Producteurs de Fleurs et d'Essence de Lavande du Département de Vaucluse et des Régions limitrophes*, published in March this year and dealing specially with the fair at Digne on October 1st 1921, the normal prices for lavender oils ought to be between 90 and 120 Francs, if it is taken into consideration that the pre-war figures for medium qualities ranged from 30 to 40 Francs per kilo. The author tries to prove that the costs have trebled and that the selling prices ought to go up in proportion. The costs of gathering (from 4 to 7 Francs per 100 kilos before the war) amounted to 25 Francs in 1919 and have sometimes exceeded 50 Francs in 1920. Last year, the manufacturers declared that, owing to the general depression and the sluggish sales, they would rather take no flowers at all than pay more than 10 to 12 Francs. The gatherers knew this and some of them were willing to work nevertheless, but they were few in number. The owners of the lavender districts wanted more hands, however, and could only get them through paying higher wages. 25 Francs per 100 kilos had to be paid, but even then there were perhaps only 20 gatherers, where 200 were required. As the depopulation in the mountainous districts of Sault has reached about 20 per cent., as per the latest estimations, one will have to reckon with a shortage of labourers in the future.

The costs of keeping the lavender plants in good condition and those of transport of the flowers have likewise trebled. Up to 500 Francs have been paid for working 1 hectare of wild lavender with 4 animals, a price which is out of all proportion, but if one takes it that in some districts only 1/2 hectare can be worked daily by two men with four animals, a cost of 150 to 200 Francs per hectare would seem justified. The wages of labourers and drivers and the cost of the fodder have risen from 7 to 25 and even 30 Francs in the mountains. The prices of the necessary implements have also trebled.

The same is the case with the costs of distillation and the general expenses. An ordinary still holding 300 litres cost before the war from 400 to 500 Francs, whereas already some time ago from 1200 to 1800 Francs had to be paid. Coal has risen from 50 to 500 Francs per ton plus 200 to 250 Francs for transport. The wages of the stokers have trebled and the amount of work done has gone down. Taxes and other expenses have risen too and there does not seem to be any chance of reduction.

Finally it is stated that, contrary to the estimation of last year's crop at 150000 kilos, the total turnover on all the different fairs had not even reached 100000 kilos and that there was very little oil left in the hands of the distillers.

A. Chiris[1]) reports, on the strength of his own investigations, on the differences presented by lavender oils obtained by open fire and by steam distillation. According to his ideas, the rotatory power of lavender oils distilled by open fire grows in absolute value with the ester contents. It is known[2]) that oils distilled by steam under otherwise similar conditions generally contain a higher percentage of esters than those obtained by open fire. Chiris points out that a high ester content is not always a criterion for the quality of the oil. Of two oils, one distilled by open fire and having 45.57 per cent. of esters, and the other oil, steam-distilled, having 52.65 per cent. of esters, he preferred the former, as being superior in aroma. As regards solubility and density, lavender oils distilled by steam are less soluble in 70 per cent. alcohol (not soluble in 3 vols.)[3]) and of greater density (d often more than 0.9) than oils distilled with water. As the indications of the United States Pharmacopœia (ninth edition) regarding density ($d_{25^\circ}^{25^\circ}$ 0.875 to 0.888) and solubility (soluble in 3 vols. 70 per cent. alcohol) are exact only for the latter kind of oils, it ought to be revised, as nowadays the majority of lavender oils are distilled by steam.

In connection with the second Lavender Congress, held at Digne on October 1st last year, as mentioned before, Lautier Fils and Roure-Bertrand Fils published a paper each on lavender oil[4]). Lautier Fils tried to decide the question whether the quality of a lavender oil depends on its ester content. For this purpose, three samples of lavender grown in the same district, Saint André de Neouilles, were distilled under identical conditions; *viz.*, 100 kilos of flowers, under a vapour pressure of 7 kilos, for 45 minutes[5]): — a) dry wild lavender, distilled 15 days after collection, b) fresh wild

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[1]) *Perfum. Record* **12** (1921), 404. — [2]) Comp. also our experiments, *Report* April 1907, 64. — [3]) These indications are not generally valid, as we have repeatedly distilled lavender oils by steam in the South of France which dissolved in 3 vols. of 70 per cent. alcohol. — [4]) *Perfum. Record* **12** (1921), 342. — [5]) This indication is of no value, as the pressure sinks at once to that of the outer atmosphere, if the still is in connection with it through rising-tube and condenser.

lavender immediately after collection, c) fresh cultivated lavender immediately after collection. The mean of a large number of analyses of the oils obtained gave the following results: —

Lot.	Density at 15°.	Solubility in 70 per cent. alcohol.	α_D.	Esters as linalyl acetate.
a	0.894	5 vols. with difficulty	5° 45′	56.4 per cent.
b	0.889	3 „	7° 20′	50.8 „ „
c	0.887	3 „	7° 50′	52.1 „ „

The three oils were submitted to distillation with a current of steam under reduced pressure, giving the subjoined results: —

(a) essential oil 79, resinous residue 21 per cent.
(b) „ „ 92, „ „ 8 „ „
(c) „ „ 96, „ „ 4 „ „

The resinous residues hat little odour, but gave the following percentages of ester: — (a) 65.4, (b) 62.3, (c) 62.6.

The authors conclude from these results that the figures representing the total ester content are misleading and that it would be necessary to deduct the ester content of the inodorous resinous residues, when the real percentages of ester would be: — (a) 42.7, (b) 45.8, (c) 49.6[1]).

It further results from the experiments that lavender which has been piled up to await distillation always gives a false titration, as resins with high ester content are formed by oxidation at the expense of the essential oil. According to Lautier Fils, the essential oils drawn from such flowers possess neither body nor fineness, although they are pure and have high titration figures for esters. They say that the value of lavender oil depends upon its "body" and upon its "bouquet", which had nothing to do with the percentage of esters, and that oils from the Alps with only 26 per cent. of esters were often far more valuable on account of their "bouquet", than other products with 45 per cent.[2]).

The authors come to the following conclusions, which do not contain anything new: — Bouquet and body are two distinct factors. The body is approximately indicated by the ester titration. Absence of artificial esters must be ensured, in order that the titration figures should be genuinely indicative of value and purity. — There is no clear answer, however, to the question put in the beginning.

We would say that these investigations do not alter the fact that, generally speaking, the value of lavender oils depends upon the percentage of esters. The more careful and appropriate the distillation of the lavender oil, the higher the percentage of esters and the less damage is done to the bouquet.

The paper from the Roure-Bertrand Fils Laboratories[3]) contains extensive, though not altogether new details regarding the distillation, composition, analysis and adulteration of lavender oils. The best lavender oils are obtained, if due attention is given to the following points: — 1) When distilling by direct heat, the flowers ought not to be soaked in water beforehand. The still must not be filled with too much water, as an excess of water diminishes the yield of oil and impairs its quality. 2) The distillation

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[1]) The authors seem to have overlooked that a second steam distillation must needs cause a further saponification of esters and an alteration of the oil. It is not stated whether the distillation was carried out under ordinary pressure or *in vacuo*. — [2]) This has been pointed out already by Birckenstock. Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. III, p. 428. — [3]) *Perfum. Record* 12 (1921), 344.

should be carried through as quickly as possible (within an hour). 3) In consequence special stills with wide neck and wide steam-pipes must be used. 4) The oil passing over has to be cooled well, as cold water dissolves less oil than warm water.

In order to obtain a uniform good product, growers ought to combine and distil the oil in joint distilling plants.

A report has been published on the meeting of the Lavender Commission, held on May 17th, 1921, in the French Ministry of Commerce, containing the suggestions and propositions made by lavender growers, merchants and industrials. The Commission, however, has not arrived at a definite solution of all the questions concerning lavender[1]).

Lautier Fils[2]) examined a lavender oil of the following constants: — d_{15° 0.894; α_D — 4° 35′; soluble in 3 vols. of 70 per cent. alcohol; ester v. 48.8. In their opinion it had been adulterated with lauric ester, obtained apparently from the residues of cocoa butter manufacture, and small quantities of terpenyl acetate.

According to Humbert[3]), the sub-species of *Lavandula fragrans* and *L. delphinensis*, created by Jordan, cannot be considered as distinct species, but merely as two extreme forms of variation in accord with the local conditions of habitat. Whereas the xerophilous *Lavandula fragrans* predominates in the sunny South of France and on the dry crests of the low mountains, the more moisture-loving *L. delphinense* thrives in the North, or in the higher valleys and higher mountains, where mists and rain are less rare, or again in the shadow of forests. Thus the Luberon shows on its arid brows (calcareous, of the lower Cretacean system), towards 1000 m. high, the most xerophil forms. But on descending from the summit towards the north, one meets on the slopes, less exposed to the sun and principally towards the base, where the soil is no longer puroly calcareous, but a soft Miocene formation and more hygroscopic, the whole gamut of transitions to forms presenting the maximum lengthening of axes and enlargement of the leaves. The transformation of one form to the other can be proved experimentally by planting the seed of the xerophil type in a damper soil or climate than the original station, or *vice versa* with the other type. The plant called *L. Faucheana*[4]) by Briquet and Rouy is also only a form of variation.

It is otherwise with *L. pyrenaica*, DC., which plant, found in the eastern Pyrenees, is distinguished by the much greater size of its principal bracts, which are as broad as long and almost conceal the calyx. The flowers are a little larger and the inflorescence appears bigger than that of *Lavandula officinalis*. The vast colonies of *L. Pyrenaica* begin where spike ceases and almost reach the summit of the mountains.

Very seldom, in altitudes of from 800 to 1500 m., the white variety of lavender occurs. It was found on the Mount Angèle near Nyons, in the neighbourhood of Saturnin-les-Apt, on the Ventoux and near Ribiers. The corolla was white in each case, the calyx either blue, red or white. In order to obtain the essential oil of this highly fragrant species, A. Chiris[5]) tried to cultivate the plant from seeds. But only a few seedlings had white flowers, those of the others being mostly very pale. The oil obtained from the latter surpassed the ordinary lavender oil in ester content and aroma[6]).

It results from Humbert's explantions that the bracts and bracteoles are of special importance for the recognition of the different species and varieties of lavender. J. Gattefossé[7]), in an article on French lavender and its hybrids, publishes six pictures

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[1]) *Parfum. moderne* 14 (1921), 153. — [2]) *Perfum. Record* 12 (1921), 343. — [3]) *Perfum. Record* 12 (1921), 252. — [4]) This type is not mentioned in the *Index Kewensis* up to 1910. — [5]) *Perfum. Record* 12 (1921), 405. [6]) There are no further details. — [7]) *Parfum. moderne* 14 (1921), 207.

of such bracts and bracteoles of *Lavandula officinalis,* Chaix, *L. latifolia,* Vill. and *L. pyrenaica,* DC. and their hybrids, taken from the *"Office national des Matières premières végétales".* According to Humbert, the hybrids of lavender and spike are more widely distributed than it was hitherto believed. Very frequent is the hybrid *"Lavandula latifolia < officinalis",* in which the properties of *L. officinalis* preponderate, so that the gatherers do not know how to distinguish it from the true kind. The other hybrid, *L. latifolia > officinalis,* so-called "lavandin", resembling more *L. latifolia,* is better known to the distillers and avoided by them. Perhaps the lavender-fields in England and in Pornichet (Loire-Inférieure), which both yield oils of a low ester percentage, are cultivations of the hybrid *"L. latifolia < officinalis".*

Humbert states further that *Lavandula Burnati,* Briq. of the Maritime Alps and *L. hortensis,* Hy.3) resemble the "lavandin", whereas *L. Spica-latifolia,* Albert, of the Var and *L. Burnati* var. *Fouresii,* Coste, of the Causses de l'Aveyron, are more similar to *"A. latifolia < officinalis".*

As regards two hybrids of *Lavandula latifolia,* Vill. and *L. officinalis,* Chaix, see page 118 of this *Report.*

Oil of Lavandula Stoechas. — As results from the investigations of Roure-Bertrand Fils1), the oil of *Lavandula Stoechas,* L.2), described by us some years ago and which we afterwards designated as originating from *L. dentata,* L.3), came in reality from *L. Stoechas* after all. The confusion was due to the fact that we had originally received (1905) from Spain the flowers of the real *L. Stoechas,* whereas the second time (1915), when we asked again for the same kind, in order to have the plant determined by a botanical authority, the flowers of *L. dentata* were sent us by mistake. The sender maintained, however, that in either case the flowers had been taken from the same plant. — Roure-Bertrand Fils state that the oils obtained by them in different years (1906) and 1921) from French *Lavandula Stoechas* differed verry little from one another and from the oil distilled by us (in 1905 from Spanish material), the constants being: — d_{15° 0.945 to 0.948, $\alpha + 47^\circ$ to $+ 49^\circ 56'$, acid v. 0.69 to 0.93, sap. v. 8.40 to 18.67, ester v. 7.71 to 17.74, ester v. after acetylation 47.14, soluble in 5 vols. and more of 60 per cent. alcohol. The principal constituents of the oil are *d*-camphor (semicarbazone, m. p. 238°), *d*-fenchone (oxime, m. p. 165°). Besides, fenchyl alcohol and perhaps terpineol and a phenol seem to be present.

In order to obtain pure fenchone, the authors oxidized the oil with nitric acid and heated the product of the reaction repeatedly with 10 per cent. aluminium chloride. The resulting fenchone had the following constants; m. p. $+3$ to 5°, d_{20° 0.9443, $\alpha_{D23^\circ} + 54^\circ 34'$, n_{D21° 1,4625, m. p. of the semicarbazone 174 to 176°.

Roure-Bertrand Fils publish simultaneously an illustrated extensive botanical study by A. Camus regarding *Lavandula Stoechas* is, like rosemary, according to its whole structure a xerophilous plant which can stand a good deal of drought. It thrives on arid slopes, exposed to the sun, on heaths and steppes, frequently together with *Cistus* and *Calycotome* species, along the coast of the Mediterranean from Gibraltar to Asia Minor, on the Canaries, in Madeira, Portugal, Spain, Menorca, Sardinia, France, Corsica, Italy, the Balkans, Crete, Syria, Palestine, Morocco, Algeria and Tunis. *Lavandula dentata,* however, does not occur in France, but only in the coastal regions of part of the Mediterranean countries, such as Spain, Morocco, Algeria and perhaps southern Italy.

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1) *Bull. Roure-Bertrand Fils,* Oct. 1921, 3. — 2) Comp. *Reports* October 1905, 10; April 1908, 62. — 3) *Report* April 1915, 28.

Lemongras Oil. — Two samples of this oil was forwarded to the Imperial Institute from Seychelles. One of these samples was stated to have been obtained from *Andropogon Schoenanthus,* L. = *Cymbopogon citratus,* Stapf, which has been grown in Seychelles for a long period. The oil had the following constants: — $d_{15°}^{15°}$ 0.883, $\alpha_{D20°}$ — 0° 12′, $n_{D20°}$ 1.486, insoluble in 70 per cent. alcohol, practically soluble in 0.9 vol. 80 per cent. alcohol at 15°, becoming turbid on dilution; citral, determined by the bisulphite method, 78.5 per cent. The oil is therefore of similar character to the West Indian lemongrass oil. The sample was valued in London at about 6 d. per oz., when commercial lemongrass oil was quoted at 8 d. per oz. (February 1919).

The second sample was stated to have been derived from a variety of lemongrass *(Cymbopogon flexuosus?)* introduced into the colony from Cochin in 1911. The golden-yellow oil showed an odour resembling that of lemongrass and also that of citronella oil. The constants were: — $d_{15°}^{15°}$ 0.898, $\alpha_{D20°}$ — 10° 12′, $n_{D20°}$ 1.484, insoluble in 70 per cent. alcohol, soluble in 1 vol. 80 per cent. alcohol at 15°, be coming slightly turbid with 3 vols.; citral, 38 per cent. (bisulphite method); geraniol, 20.5 per cent. These data show that the oil differs markedly in composition from the East Indian oil and suggest that this "lemongrass" oil is not derived from *Cymbopogon flexuosus,* but from some other species. Possibly it may ever be a mixture of lemongrass and citronella oils.

We gather from and English periodical[1]) the following statements concerning the so-called West Indian lemongrass oil derived from *Cymbopogon citratus,* Stapf which is known to differ from the East Indian oil by its low solubility in alcohol. The oil was originally distilled in Travancore and came to England via Cochin for the first time in 1832. When later the industry extended northwards to Malabar, Calicut became the centre of distribution. Recently, the oil is being distilled in Assam and Java. Before the war, from 2000 to 3000 cases, each containing one dozen quart bottles of oil (each 1.236 litres) were exported annually from Cochin to Bombay as well as to New York, Hamburg, and London.

Oil of Leptospermum flavescens. — In the oil of *Leptospermum flavescens* var. *citratum,* Challinor, Cheel and Penfold[2]), some years ago, proved the presence of a phenol yielding a benzoate of the m. p. 67°. This phenol, termed *leptospermol,* has now been investigated closely by Penfold[3]). The amount of the phenol in the oil varied according to the different localities from which the material was collected, and ranged between 0.75 and 8.0 per cent. The leptospermol ($C_{14}H_{20}O_4$?) was abstracted from the oil by shaking with a 3 per cent. caustic soda solution and was a somewhat viscous liquid, almost colourless, with a pleasant and characteristic odour, and the following constants: — b. p. 145 to 146° (10 mm.), 275 to 278° (770 mm., uncorr.), $d_{20°}$ 1.073, $\alpha \pm 0$, $n_{D20°}$ 1.5000. In alcoholic solution, it gave with ferric chloride a brilliant distinctive orange-red coloration; with copper salts, an intease blue coloration. Derivatives of the phenol were not obtained. The phenol bears a very strong resemblance to the phenol tasmanol[4]) found in various eucalyptus oils, but differed therefrom by the refractive index and the boiling-point under reduced pressure.

Oil of Leptospermum grandiflorum. — From the leaves of *Leptospermum grandiflorum,* Lodd., a myrtacea growing in the river-beds in New South Wales, A. R. Penfold[5]) obtained 0.61 per cent. of a rather viscous, dark brown oil. After shaking with dilute

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[1]) *Perfum. Record* **12** (1921), 50. — [2]) Comp. *Report* **1919**, 34. — [3]) *Perfum. Record* **12** (1921), 336. — [4]) Comp. *Report* **1916**, 30. — [5]) *Journ. Proceed. of R. S. of N. S. W.* **54** (1921), 197. Acc. to *Bull. Roure-Bertrand Fils,* October **1921**, 159.

sodium hydroxide solution the oil exhibited the following constants: — d_{15° 0.9324, $\alpha_D - 2^\circ 42'$, n_{D20° 1.5048, ester v. 7.2, ester v. after acet. 40.98; insol. in 10 vols. of 80 per cent. alcohol. By repeated fractionation of the oil in presence of sodium, under 10 mm. pressure, the auther obtained the fractions: — 123 to 125° (d_{15° 0.910, $\alpha_D - 6.2^\circ$, n_{D20° 1.4967) and 129 to 132° (d_{15° 0.921, $\alpha_D + 0.72^\circ$, α_{D20° 1.5063). These two fractions, which agreed in their constants fairly with aromadendrene and eudesmene[1]), gave likewise the colour reaction of these sesquiterpenes with bromine and with sulphuric acid[2]). In addition, the oil contained, besides a small amount of phenolic bodies, a sesquiterpenic alcohol, which the author was unable to describe more closely.

Oil of Leptospermum odoratum. — On distilling the leaves and twigs of *Leptospermum odoratum*, Cheel, a plant likewise occuring in the valleys of New South Wales, A. R. Penfold[3]) obtained on the average 0.75 per cent. of a yellow oil with an odour reminding of terpenes and roses. Its constants differed according to the time of collecting (August, 1917, May and October, 1920) and ranged as follows: — d_{15° 0.9163 to 0.9280, $\alpha_D - 16{,}32$ to -33.02°, n_{D20° 1.4960 to 1.4990, ester v. 5.6 to 7.2, ester v. after acet. 57.00 to 91.93, sol. in 10 vols. of 80 per cent. alcohol, in one case insoluble in 80 per cent. alcohol. In addition to combined acetic acid, the oil contained above all butyric acid in combined state. In the fraction b. p. 60 to 90° (10 mm.), α- and β-pinene were proved to be present by means of characteristic derivatives[4]). The fraction 125 to 140° (10 mm.), one-half of the oil, contained nearly equal parts of eudesmene and aromadendrene which were identified by means of their constants and their colour reactions[5]). This natural eudesmene differed from the synthetical dextrorotatory preparation[6]) by its optical rotation of −53°. From the solid distillation-residue (10 to 15 per cent. of the oil), there was obtained, by crystallisation from dilute alcohol, eudesmol, m. p. 79 to 80°, b. p. 156° (10 mm.), $[\alpha]_{D20^\circ} + 31.80^\circ$. Furthermore, the oil appeared to contain about 2 per cent. of an alcohol not further dealt with, which gave rise to the rose-like odour of the oil.

Oil of Lindera sericea. — A. Spann[7]) reports that according to official Japanese statistics an essential oil is distilled from the lauracea *Lindera sericea*, Blume (Kuromoji[8])). The producing districts, Hiogo *ken*, Shimane *ken* and Hiroshima *ken*, are in the southern part of the main island Honshiu. In 1915, 9438 kin of oil were obtained, representing a value of 9880 yen.

Machilus Oil. — Seisi Takagi[9]) obtained from the wood shavings of the Formosan Lauracea *Machilus Kusanoi*, Hayata[10]), on distillation, a pale yellow, viscous oil with the constants: — $d_{4^\circ}^{27^\circ}$ 0.9815, $[\alpha]_{D27^\circ} + 18.20^\circ$, acid v. 0, sap. v. 0, sap. v. after acet. 50.21. On fractionation under 5 mm. pressure, 120 g. of the oil gave 6 g. oil b. p. 125 to 140°, 42 g. b. p. 140 to 149°, 25 g. b. p. 149 to 159°, 9 g. b. p. 156 to 170° — these three

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[1]) Cf. *Reports* April **1902**, 31; October **1913**, 59. — [2]) In the literature, colour reactions are only given for aromadendrene (cf. Baker and Smith, *A Research on the Eucalypts*, 2nd ed. p. 417; Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed. vol. III, p. 275) but not for eudesmene. — [3]) *Journ. & Proceed. of R. S. of N. S. W.* **54** (1921), 197. Acc. to *Bull. Roure-Bertrand Fils*, October **1921**, 159. — [4]) Details in this respect are missing in the abstract. — [5]) Cf. the footnote above, with *Lept. grandifl.* — [6]) Cf. *Report* October **1913**, 59. — [7]) *Der Tropenpflanzer* **24** (1921), 167. — [8]) Details concerning the Kuromoji oils obtained from the leaves and other parts of the plant are to be found in Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 502. — [9]) *Journ. pharm. Soc. Japan* **1921**, No 473 (2nd communication). From a copy kindly forwarded to us. Unfortunately, we hitherto did not come across either the first communication or an abstract thereof. — [10]) Is not mentioned in the *Index Kewensis* of 1910.

fractions solidify to a crystalline mass —, and 10 g. of a viscous oil, b. p. 170 to 185°. Repeated crystallisation of the solid fractions yielded a body $C_{15}H_{26}O$, *machilol;* m. p. 79 to 80°, b. p. 160° (14 mm.), $[\alpha]_{D25°} + 42.87°$. On treatment with acetic anhydride and sodium acetate the body is acetylated but partly; neither is formed a phenylurethane with phenyl*iso*cyonate nor a benzoate according to Schotten-Baumann. Reduction with platinum black and hydrogen yielded dihydromachilol $C_{15}H_{28}O$, m. p. 82 to 83°, b. p. 157 to 158 (14 mm.), $[\alpha]_{D18°} + 16.43°$. By oxidation with potassium permanganate, machilol passed over into dihydroxymachilol, or machilene glycerol $C_{15}H_{28}O(OH_2 + H_2O$, m. p. 110°, $[\alpha]_{D13°} - 25.91°$; monobenzoate, m. p. 142°. This body proved to be identical with α-dihydroxyatractylol which the auther obtained, in addition to β-dihydroxyatractylol (m. p. about 78°, $[\alpha]_{D13°} + 24.68°$), on oxidising atractylol by the same reagent. Hence, machilol is a bicyclic, tertiary sesquiterpene alcohol.

When machilol was heated with formic acid, machilene $C_{15}H_{24}$ resulted; b. p. 120° (3 mm.), $d_{4°}^{23°}$ 0.9109, $[\alpha]_{D23°} + 58.73°$, $n_{D23°}$ 1.51257; Liebermann's reaction: first blue, then green, and after some standing dark blue. On reducing machilene with hydrogen and platinum in glacial acetic acid, tetrahydromachilene $C_{15}H_{28}$ was formed; b. p. 132° (11 mm.), $d_{4°}^{19°}$ 0.8964, $[\alpha]_{D10°} + 37.04°$, $n_{D10°}$ 1.48645.

Machilene is no uniform body, but a mixture of probably two isomerides, for on abstracting water from machilol by weaker-acting reagents, an isomeride of machilene is formed with higher rotatory power (α_D about $+ 100°$).

On reducing atractylene (b. p. 108 to 109° [3 mm.], $d_{4°}^{13°}$ 0.9189, $[\alpha]_{D13°} + 78.35°$, $n_{D13°}$ 1.51795) catalytically, tetrahydroatractylene is formed (b. p. 129 to 130° [10 mm.], $d_{4°}^{11°}$ 0.9030, $[\alpha]_{D12°} + 36.99°$, $n_{D12°}$ 1.49589), a liquid with a feeble but pleasant odour.

Since the tetrahydro derivatives of machilol and atractylol agree very closely in their qualities, Takagi ascribes to atractylol (or atractylene) and to machilol (or machilene) the same carbon nucleus, both bodies differing merely by the position of the double linking and the hydroxyl group.

Massoi Bark Oil. — According to the Imperial Institute[1]), the Massoi bark from the Fiji Islands and New Guinea and sold on the Singapore market, comes from *Cinnamomum pedatinervium,* Meissn. (identical with *Massoia aromatica,* Beccari [?])[2]).

Milfoil Oil. — An extensive publication on this oil has been published by R. E. Kremers[3]). The crude material, *Achillea Millefolium,* L. serving for the investigation was collected from the middle of June to the middle of July, freed carefully from foreign matter, and dried immediately at the open air. About 1200 pounds of fresh herb weighed after three days' drying 420½ pounds or 190.7 kilos, and yielded 892 g. of oil, or 0.467 per cent. of the dry herb. This exceptionally high[4]) yield of essential oil was arrived at by cohobating the distillation-water, thus obtaining in addition to the principal oil, 21 per cent. of "water oil", calculated on the former oil.

Firstly, the "water oil" was subjected to fractional distillation. The fractions, b. p. between 64 and 90°, proved to contain formaldehyde (by its odour, and Schiff's reagent), methyl alcohol (methyl salicylate, formaldehyde, and *3,5*-dinitrobenzoic methyl ester), ethyl alcohol (iodoform reaction), acetone (reaction with sodium nitroprusside and iodine potassium iodide), furfural (aniline acetate), borneol (m. p. 203 to 204°).

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[1]) *Bull. Imp. Inst.* 19 (1921), 338. — [2]) As to the still doubtful origin of the Massoi bark of commerce see Gildemeister and Hoffmann, *The Volatile Oils,* 2nd edition, vol. II, p. 498. — [3]) *Journ. Americ. pharm. Assoc.* 10 (1921), 352. — [4]) From dried blossoms once even 0.485 per cent. oil were obtained, from fresh blossoms, as a rule, 0.07 to 0.25 per cent. Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. III, p. 617.

The constants of the principal and the aqueous oil (together with those observed by Miller[1]) in 1916) were as follows: —

	Principal oil		Aqueous oil	
	1916	1919	1916	1919
d_{17°	0.915	0.913	d_{25° 0.939	0.948 and 0.959
Acid value	7.24	4.27[2])	37.0	—
Ester value	2.2	5.65[2])	7.6	17.7
Sapon. value . . .	9.44	10.92[2])	44.6	—
Ester v. after acet.	23.5	17.8	51.8	50.9

These figures show that the water oils contain more free acid, more esters and more free alcohols than the principal oils. The following constituents of the cohobated oil were identified: — A valeric acid (in all probability; silver salt), a large quantity of impure borneol, furfural (aniline acetate reaction), and traces of eugenol (benzoate, m. p. 69 to 70°).

The main oil was separated by fractionation, first under atmospheric pressure, into 10 fractions boiling between 85 and 174°, then under 30 mm. pressure, into 10 more fractions boiling between 75 and 125°. Miller[3]) had proved formerly the presence in these fractions of following bodies: — valeric, salicylic and butyric acids, aldehydes, pinene, limonene, camphor, borneol, and cineole. In addition to these constituents which, except limonene, were also identified by Kremers, the latter author succeeded in identifying nopinene (nopinic acid, m. p. 126°; nopinone semicarbazone, m. p. 188°). The constants of a saponified fraction of the b. p. 90 to 95° pointed to the presence of thujone (d_{25° 0.929, α — 3.0°, n_{D25° 1.4588). The tribromide (Wallach) showed the m. p. 121°; the semicarbazone was readily formed, but was either a mixture of the derivatives of α- and β-thujone, or of thujone with that of another ketone.

From 100 g. of a fraction boiling above 140°, Kremers obtained 35.5 g. of a blue oil, containing azulene, b. p. 135 to 136° (1.1 mm.), and 59 g. non-blue oil. With alcoholic picric acid solution, azulene yielded instantly the picric acid addition compound. After removal of the azulene by means of phosphoric acid, the oil was fractionated (pressure, 5 to 0.1 mm.) into 8 fractions boiling between 80 and 180°. From the portions boiling between 100 and 115° (0.5 mm.) the author obtained, by distillation with sodium, a fraction with the constants: — b. p. 105 to 110°, d_{20° 0.916, α — 13.75° (100 mm. tube), n 1.4990, mol. refr. 65.4, which yielded a benzylamine base, m. p. 172 to 173°, and a hydrate, m. p. 94 to 95°. The presence of caryophyllene, therefore, must be considered as proved.

As a supplement to Kremers' notes on the work of Miller on milfoil oil, we add the following statements culled from Miller's paper, the copy of which reached us only recently. E. R. Miller[3]) obtained by steam-distillation partly from the entire (fresh or dried) plant, partly from the flowers or the leaves of *Achillea millefolium*, L. cultivated near Madison a series of oils, all of which were dark blue. The flowers yielded more blue oil than the leaves. Distillation of the lower two-thirds of the plant is unprofitable. Drying of the plant apparently produces no change in either the quantity or quality of the oil. Apparently, there exist some definite relations between yield on one hand and density and refractive index on the other. As stated above, Miller separated the oil into various fractions and proved the existance of following constituents in the oil: — *l*- and *d*-pinene (nitrosochloride, m. p. 102 to 103°; nitrolpiperidin, m. p. 119°), *l*-limonene (?)

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[1]) Cf. *Bull. 785, University of Wisconsin.* See also further below on this page. — [2]) These figures do not agree with each other. — [3]) *Bull. Univ. Wisconsin* No. 785.

(odour and density of corresponding fractions, no nitrosochloride being obtained), *l*-borneol (m. p. 202 to 203°; acetate, m. p. 29°; phenylurethane, m. p. 139°), bornyl acetate and other borneol esters, *l*-camphor (oxime, m. p. 119°; semicarbazone, m. p. 235 to 236°), cineole (resorcinol compound; iodole derivative, m. p. 106 to 107° instead of 111 to 112°), salicylic acid (colour reaction with ferric chloride), aldehydes (presumably two, Schiff's reagent), formic, acetic, butyric (?), and *iso*valeric acids (silver salts), a non-volatile acid or a lactone, and a blue constituent of high b. p. (145° at 15 mm.).

Monarda Oils. — A series of methoxyl estimations in monarda oils undertaken partly with unchanged oils, partly after removal of the phenols in the hope that this constant would prove characteristic, has been published by D. C. L. Sherk[1]). In the oils of *Monarda punctata*, the content of methoxyl amounted to 0.11 to 0.36 per cent. The non-phenolic parts of the oils differed in their methoxyl value hardly from the original oil. Hence, on the separating of the phenols a methoxylated body must have dissolved in the aqueous alkali. Such a body is the monomethyl ether of thymohydroquinone, since the dimethyl ether and thymol methyl ether, otherwise constituents of the oil, are non-phenolic bodies, *i. e.*, insoluble in alkali. Sherk was able to prove that the alkaline extract of an oil from *Monarda fistulosa* contained a pale reddish oil with 1.14 per cent. methoxyl and leaving on distillation a tarry residue with 0,95 to 1,17 per cent. methoxyl. The part of the oil extracted from the alkaline liquid by means of ether contained, in addition to carvacrol, thymohydroquinone.

From an oil of *Monarda punctata*, the thymol of which had been removed for the greater part by freezing, Sherk obtained crystals of thymohydroquinone and a black, tarry residue with 0.61 to 1.48 per cent. methoxyl. This residue consisted for one-third of thymohydroquinone, m. p. 141°, which was isolated therefrom by fractional distillation.

It is well-known that the essential oils obtained by redistillating the distillation-water of essential oils show properties differing from those of the principal oil. In the most cases, especially the specific gravity of the latter oil is lower than with the "water oil", as the water-soluble constituents of essential oils show, as a rule, a higher density than the bodies insoluble in water. As we gather from a paper by E. R. Miller[2]) on "Redistillation of aqueous distillates resulting from the production of volatile oils", the specific gravity of the principal oil from *Monarda fistulosa*, L. amounted to 0.9280, with the "water oil" of the same plant, to 0.9700. Wormwood oil, however, behaved according to Miller, differently, since the "water oil" was lighter owing to the content of thujone. The yield of wormwood "water oil" ranged between 6 and (?) 37 per cent. of the aqueous distillate, according to the maturity of the plants under investigation.

Oil of Mosla grosserata. — Y. Murayama[3]) discovered in the oil of *Mosla grosserata*, Maxim., a new terpene, moslene (comp. p. 50 of this *Report*).

Oil of Mosla Hadai.—As we hear from Asahina, the oil[4]) investigated some years ago by Y. Murayama did not come from *Mosla japonica*, Maxim., but from *Mosla Hadai* Nakai[5]). (Comp. also lower down.)

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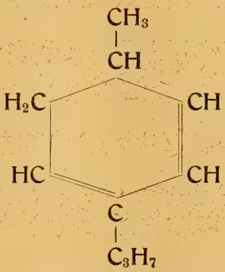
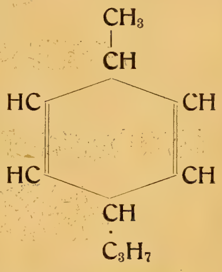
[1]) Fritzsche Bros. Fellow, 1919/20. *Journ. Americ. pharm. Assoc.* **10** (1921), 417. — [2]) *Midland Druggist and pharm. Review* **54** (1920), 146. — [3]) *Journ. pharm. Soc. Japan* **1921**, No. 475. — [4]) Comp. *Report* April **1910**, 78. — [5]) The *Index Kewensis* does not mention it up to 1910.

Oil of Mosla japonica. — Since Hada's discovery of thymol in the oil of *Mosla japonica*. Maxim. this plant has been cultivated in Japan with the object of obtaining this phenol. On investigating the terpene fractions of the oil[1]), Y. Murayama[2]) found a new terpene named by him *moslene*. This body was found in a fraction with the b. p. 59 to 60° (10 mm.) or 173 to 175° (ord. pressure) obtained from an oil after the thymol had been removed with alkali. The fraction, which was not quite free from oxygen, showed some resemblance with the terpene crithmene obtained by Francesconi and Sernagiotto[3]) from Italian samphire oil, and had the following constants: — d_{18° 0.8528, n_D 1.48228; nitrosochloride m. p. 111°, nitrolpiperidide m. p. 142 to 143°, nitrolanilide m. p. 126 to 128°, dihydrochloride m. p. 52°, nitrosate m. p. 114°.

On treatment of the nitrosochloride, in alcoholic solution, with sodium, a body $(C_{10}H_{13})_2N_2O$ resulted; yellow needles, m. p. 52 to 53°; sometimes, a less soluble substance $(C_{10}H_{13})_2N_2$, orange-yellow leaflets, m. p. 85 to 87°, was formed, which proved to be identical with azo-*p*-cymene (m. p. 87°); formation of the latter by reduction of *p*-nitrocymene. The identity of the yellow body (m. p. 52 to 53°), too, with azoxy-*p*-cymene, is, in Murayama's opinion, established, in so far as the yellow body and azoxy-*p*-cymene, on reduction, both give rise to the identical benzidine derivatives $([C_{10}H_{13} \cdot NH_2 \cdot HCl]_2$, decompos. p. 292°).



I. 1 : 2-Dihydrocymene.



II. 1 : 4-Dihydrocymene.

According to Murayama, moslene, therefore, is a dihydrocymene, with two double bonds located most probably in the benzene nucleus. Since amongst the five isomerides complying to these conditions three are known, *i. e.*, α-terpinene, γ-terpinene, and α-phellandrene, moslene appears to be constituted as stated in one of the above formulæ.

Mustardseed Oil. — Up to now it was only known that the insoluble deposits, forming sometimes in mustardseed oil, consisted of an orange yellow compound, containing carbon, nitrogen, hydrogen and sulphur. H. Kunz-Krause[4]) investigated this compound more closely. He comes to the conclusion that it is not a uniform body, but is composed of allylamine sulphate, soluble in water, and *pseudo*-sulphocyanogen, insoluble in water. In addition to these two chief compounds, there are present most likely small quantities of xanthogenic acid derivatives, *iso*-sulphocyanic acid and allyl-substituted urea. As the constituent of the deposit which could be washed out with water, smelled distinctly of mustardseed oil, after having been stored over caustic lime for several months, the author thinks that the insoluble part decomposes and splits off allyl mustard oil. It is probable that a solid polymeride of *iso*-sulphoallyl cyanide $(S = C = N - C_3H_5)_n$ forms, perhaps in combination with *pseudo*-sulphocyanogen, $C_3HS_3N_3$, formerly called per-sulpho-cyanogen[5]). The author gives as the reason for the formation of the deposit and of the other accessory compounds always present in mustardseed oil, the decomposition of three molecules of mustardseed oil in sulphur and allyl cyanide, and certain intramolecular changes of the mustardseed oil, due to

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[1]) Cf. *Bericht* (German) 1920, 42. — [2]) *Journ. pharm. Soc. Japan* 1921, No. 475. According to a reprint kindly forwarded to us. — [3]) Cf. *Report* October 1913, 94. — [4]) *Arch. der Pharm.* 259 (1921), 16. As per a reprint kindly sent us. — [5]) I. Maier, *Die ätherischen Öle*, Stuttgart 1862, p. 167.

the influence of air, light and moisture. In consequence, mustardseed oil ought to be kept always in small, absolutely dry vessels and guarded against air and light.

According to A. Cauda1), the percentage of mustardseed oil is smaller in southern districts (Sicily), than in the more northern regions (Piemonte, Forli), the content of oil being the smaller, the greater the content of fatty oil. During germination, the content of mustardseed oil, which diminishes on etiolation, remains fairly constant. Black mustardseed contained 0.284 per cent., the green germs 0.280 per cent., the etiolated germs 0.170 per cent. of essential oil, calculated with reference to air-dried substance. The test was carried out by oxidizing mustardseed oil with bromine water and depositing the sulphuric acid formed as baryum sulphate.

V. Massera2) states that the Italian Pharmacopœia, 3rd edition, contains erroneous indications for the determination of mustardseed oil. Instead of 9.5 to 10 cc. of ammonium sulpho-cyanide solution, 15 to 15.5 cc. are required3).

Neroli Oil.—See Orange Blossom Oil, p. 53 of this *Report.*

Oil of Ocimum gratissimum.—An oil of this plant originating from Mahé (Seychelles) and differing entirely in character from the oil produced in the Ivory Coast and Central Africa, has been mentioned by us in our *Report* **1919**, p. 36, where we quoted the constants. In the meantime, the plant has been identified at Kew as *Ocimum gratissimum,* L., and a sample of the oil ($d_{15^\circ}^{15^\circ}$ 0.996; $\alpha_D -12.7^\circ$; n_{D20° 1.532; phenols, 55 per cent.) was investigated by O. D. Roberts4).

After removing the free acids (0.2 per cent., probably acetic acid) and the free phenols (entirely eugenol, b. p. 252 to 253°; benzoyleugenol, m. p. 69 to 70°), an oil remained resembling in odour the oil of sweet basil, with the constants:—$d_{15^\circ}^{15^\circ}$ 0.9013; $\alpha_D -15.0^\circ$, n_{D20° 1.513, ester v., 4.5; ester v. after acet. 101.5. On distillation under 20 mm. pressure the oil yielded the fractions:—1. B. p. 70 to 85° (16 per cent. of the original oil); 2. b. p. 85 to 100° (15 per cent.); 3. b. p. 100—135° (9 per cent.). Fraction 1 consisted chiefly of ocimene (b. p. 70 to 75° [20 mm.]; $d_{15^\circ}^{15^\circ}$ 0.8029; inactive, n_{D20° 1.4855; dihydromyrcene, $d_{15^\circ}^{15^\circ}$ 0.7777; n_{D17° 1.4500; mol. refr. 47.7; tetrabromide, m. p. 88°). Fraction 2 recalled the odour of linalool; on oxidation with chromic acid mixture a citral-like odour was produced. Fraction 3 had a distinct odour of methylchavicol, but judging from the specific gravity, no large proportion of this compound was present.

The composition of the sample, therefore, is approximately as follows:—Terpenes (ocimene), 16 per cent.; phenols (eugenol), 55 per cent.; phenol ethers, calculated as methylchavicol, 5.6 per cent.; alcohols, probably linalool, 13 per cent.; esters, 0.6 per cent.; residue and loss, 9.8 per cent. The oil appears to be rather similar in composition to an oil of sweet basil of the variety *Selasih Mekah* from Java, as examined by van Romburgh5).

Oil of Ocimum viride.—A sample of the oil from *Ocimum viride,* Willd. was forwarded to the Imperial Institute from Seychelles in 1919 and revealed on examination6) the following properties:—$d_{15^\circ}^{15^\circ}$ 0.910; $\alpha_D +0.75^\circ$; n_{D20° 1.497; phenols, consisting almost entirely of thymol, 37 per cent., whereas previous samples of the oil of identical origin,

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1) *Staz. Sperim. Agrar. Ital.* **52** (1919), 544. According to *Chem. Zentralbl.* **1921**, I. 814. — 2) *Boll. Chim. Farm.* **60** (1921), 62. As per the *Chem. Zentralbl.* **1921**, IV. 391. — 3) Years ago, when discussing the Italian Pharmacopœia, we have already pointed out this mistake. Comp. *Report* April **1910**, 131. — 4) *Journ. Soc. chem. Ind.* **40** (1921), T. 164. — 5) Comp. also Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. III, p. 578. — 6) *Bull. Imp. Inst.* **18** (1921), 348.

investigated in 1917, contanied 52 to 62 per cent.[1]). Equally, the yield of oil in the present instance was less (0.2 per cent.) as compared with the former yields (0.5 and 0.45 per cent.) obtained in 1916 and 1917. It was of importance to as certain whether this low yield of oil was due to faulty distillation or whether it was due to the stage of growth or condition of the leaves. Since the oil is of importance for the manufacture of thymol, it was suggested that the conditions be determined for obtaining the largest yield of oil containing a maximum of thymol.

Olibanum Oil.—See Frankincense Oil, p. 36 of this *Report*.

Orange Blossom Oil.—According to news from the South of France, the probable result of the coming flower crop will be about one fourth of the normal average. As it is known, the trees had suffered from the severe frost in the winter 1919/20 to such an extent that part of them had to be cut down to the roots, whereas from others the largest branches had to be sawn off. These trees, of course, do not come into consideration at all for the next crop. Those, however, which in warmer places were less exposed to the frost have plenty of buds and promise fair, unless there be frosts again before the beginning of May. Nothing can be said so far as to the price of the blossoms, but after having paid 10 francs per kilo in 1920 and Fr. 12.50 in 1921, one hopes to see them this year reduced to about one-half.

W. Niemz[2]) states that the production of neroly oils in Italy, especially in Sicily, which so far had been unable to compete with the French distillates, is improving also in quality. He says that it is scarcely possible to tell any difference between Italian and French oils.

On account of our own experience we are a little more sceptical. What we have seen so far of Italian oils does not come up by far to the French qualities. This holds good even for the samples received quite recently. Apart from the odour, there is a difference in the constants. We have often had the impression that one is a little careless in the selection of the material, distilling not only flowers, but leaves, branches and unripe fruits. It is also possible that the blossoms of the bitter and the sweet orange-trees are used indiscriminately and that the state of development of the blossoms is not sufficiently taken into consideration. In France, only the fully developed blossoms of the bitter orange-tree, gathered with care, are distilled, and this accounts perhaps for the superiority of the French product.

Origanum Oil.—In our *Report* of **1918**, page 37, we quoted as a communication of the Imperial Institute[3]) the phrase: "Ordinary Cyprus oil is said to contain merely thymol" and added that this seemed to us rather doubtful. It has been found out meanwhile that the mistake was on our side, as the original English text states correctly: "Cyprus origanum oil only contains carvacrol".

Oil of Orixa japonica.—By steam distillation of the leaves and twigs of *Orixa japonica*, Thunb. *(Celastrus Orixa)*, a celastracea known in Japan as *Kokusagi*, Y. Shinosaki[4]) obtained about 0.01 per cent. of a light brown oil having a characteristic odour recalling that of the oil of *Lindera sericea*, Blume[5]). The constants were:—

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[1]) Comp. *Report* **1918**, 36. — [2]) *Deutsche Parf.-Ztg.* 7 (1921), 161. — [3]) *Bull. Imp. Inst.* **15** (1917), 306. — [4]) *Journ. chem. Ind., Japan* **24** (1921), 563. *Journ. Soc. chem. Ind.* **40** (1921), A. 560. — [5]) Hitherto, nothing is known as to the essential oil of this lauracea.

d_{15° 0.8974; $[\alpha]_D$ —4.5°; n_{D20° 1.4750; soluble in 2 vols. 80 per cent. alcohol; acid v. 0; sap. v. 37.27; sap. v. after acet. 100.3. Its principal constituents are camphene, linalool, a terpene alcohol and its ester¹).

Orris-root Oil. — The last crop of Florentine orris-root is estimated by competent people at from 250000 to 300000 kilos, a very unfavourable result. The high costs of labour do not induce anybody to having the roots dug up, the less so as there are considerable stocks from last year, owing to the sluggish demand. As these old stocks are said to amount to about 300000 kilos, there would be 300000 to 350000 (?) kilos available, altogether *i. e.* about the same quantity as has been obtained in an average crop of the last ten years. As there is very little business, the dealers try to make the consumers believe that there will be a rise, but it seems rather doubtful whether they will succeed in the long run.

Our two qualities of orris-root oil are in good demand, which proves that they have maintained their leading position in perfumery, in spite of the manifold impediments of the post-war times.

Whereas in Italy, and especially in the province of Florence, *Iris germanica,* L. and *Iris pallida,* Lam., are cultivated above all, in France *Iris florentina,* L. = *Iris alba* is grown almost exclusively, though on a smaller scale. Some few iris plantations are said to be found in the departments of Var and Bouches-du-Rhône, according to A. Roulet²). The largest plantation exists in the department of Ain, where the plant was cultivated already in 1835. It covers from 10 to 30 hectares, according to the year. Pellissier²) says that the cultivation is restricted to the small communities of Anglefort and Corbonod, comprising a distance of 10 to 15 kilometres on the right bank of the Rhône. The iris, which adapts itself to every calcareous soil, if not too fresh and too moist, thrives best on good alluvial soil. In Ain the plant is cultivated on tilled, calcareous steppe-land. Very rich soil does not suit the iris, nor should stable manure be given, as it influences the aroma of the rhizomes unfavourably. Artificial nitrogenous fertilizers do not seem to have any effect on the development of the plant, whereas potash compounds favour the aroma and the growth of the rhizomes. Others recommend on the contrary 15000 to 20000 kilos of stable manure or 8 to 10000 kilos of oil cake per hectare after the second or third rotation of crops.

Planting takes place already towards the end of August, for which purpose the young shoots of two-year-old rhizomes are kept. They have no swelling yet, but roots, and are planted 25 to 30 cm. apart in every direction and 10 cm. deep. Sometimes they are first kept in a nursery and planted out in the following autumn.

The best remedy against "iris rot"³), it is said, is to improve the soil, in case it should be too damp, and to disinfect it with carbon sulphide (200 grams per square metre).

In the department of Ain, the rhizomes are collected already in the second year, from August to October; in Tuscany, in spring of the third year. The rhizomes are not, as in Italy, first soaked in water, but cleaned and freed from the black skin by women and children. Sometimes the rhizomes are cut in pieces, 5 to 10 cm. long and 3 cm. thick. After having been soaked in water for 24 hours, they are spread on bast mats and dried in the sun or in a moderately warm stove. The yield of a two year old plantation comes up to from 5 to 6000 kilos of dry rhizomes on an average, corresponding to from 10 to 12000 kilos of fresh rhizomes.

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¹) Details are not given in the abstract. — ²) *Parfum. moderne* **13** (1920), 154. — ³) Cf. *Report* October **1915**, 65.

Palmarosa Oil. — A sample of this oil, forwarded in 1917 from the United Provinces of India, was investigated in the Imperial Institute[1]) with the following result: — $d_{25°}^{15°}$ 0.889; α_D — 0.41°; $n_{D20°}$ 1.477; sol. in 1.8 vol. of 70 per cent. alcohol; acid v. 1.6; ester v. 11.8; total alcohols, calculated as geraniol, 90.7 per cent. The oil answered nearly fully the requirements of a good commercial quality, yet it smelled slightly of lemons and had not the clean geraniol odour of highest grade palmarosa oil; possibly, the sample contained lemongrass oil.

A second sample of palmarosa oil distilled at Cawnpore contained a lower percentage of total alcohols and its aroma was not quite equal to that of the previous sample. Its constants were: — $d_{15°}^{15°}$ 0.889; $\alpha_{D20°}$ + 0.32°; $n_{D20°}$ 1.472; sol. in 1.9 vol. 70 per cent. alcohol; acid v. 0.8; ester v. 28.0; total alcohols, calculated as geraniol, 85.5 per cent.

Patchouly Oil. — Whereas the true patchouly plant of commerce, *Pogostemon Patchouli*, Pell., or *P. Cablin*, Benth., is cultivated only to a very small extent in Java, there are extensive patchouly fields in the North of Sumatra, especially near Tapa Tuan in the Atjeh district[2]). In the beginning the natives cultivated the plant, *nilam*, in order to prepare with the aid of its leaves a hair oil for their own use, and the export of the dried leaves did not begin earlier than about ten years ago. The plantations extended in the same proportion as the prices rose (at present 15 florins per picul, as compared with only 3 florins ten years back). Now they are not only restricted any more to Tapa Tuan, but are also found in the districts of Sama Dua, South-Dho, Phoa and Menke.

Before the war, France and Germany were the chief European importers of patchouly leaves. In 1913, France imported 3659 piculs and Germany 4975 piculs from Penang; in 1914, France imported 93 piculs from Singapore and 1655 piculs from Penang, whereas Germany took 2973 piculs from Penang. In addition, considerable quantities went to British India, Hongkong and, since 1911, to the United States. Japan and Canada were buyers for the first time in 1918, the former importing 259 piculs and the latter 481 piculs from Singapore.

According to a report of the Dutch Chamber of Commerce in New York[3]) the distillation of the oil has been started in Atjeh, the export centre of patchouly leaves.

Roure-Bertrand Fils[4]) examined two patchouly oils from the neighbourhood of Kotta-Radja (Sumatra), obtained by distillation of leaves and stems, and found the following constants: —

	leaf oil	stem oil
$d_{15°}$	0.9698	0.9739
α	— 52° 4′	— 54° 8′
acid v.	1.2	8.7
ester v.	6.7	1.3
„ „ after acetylation	26.13[5])	—
solubility in 85 per cent. alcohol	turbid	turbid
„ „ 90 „ „ „	up to 1 vol., turbid in 3 to 4 vols.	in any proportion

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[1]) *Bull. Imp. Inst.* 18 (1921), 342. — [2]) *Chem. and Druggist* 96 (1922), 56. — [3]) *Holland and her Colonies* 1 (1921), No. 7, p. 15. — [4]) *Bull. Roure-Bertrand Fils*, April 1921, 18. — [5]) In this case the acetylation is of very little importance, as patchouly alcohol cannot be acetylated quantitatively.

Both samples had a very fine odour, thus distinguishing themselves from the Penang (Singapore) oils. The high specific gravity seems to indicate that the plant, from which they originate, belongs to the Singapore variety[1].

Two patchouly oils of 1917 and 1919 from the United Provinces of British India, examined by the Imperial Institute[2], had the following properties: — $d_{15^\circ}^{15^\circ}$ 0.992 and 0.998, α_{D20° ? and -77°, n_{D20° 1.513 and 1.515, soluble in 0.3 vol. of 90 per cent. alcohol at 15°, acid v. 3.3 and 1.0, ester v. 4.4 and 5.3. It results from these figures that the oils have nothing in common with the Java oil and very little with that from Singapore, whereas they come very close to the distillates obtained in Europe from Singapore leaves.

Peach Oil. — Although many preparations designated as "Peach Oil" or "Peach Essence" have long been in use for flavouring purposes, it is well known that they consist for the most part of purely empirical mixtures of esters and essential oils with other aromatic substances which occur but little or not at all in the fruit whose flavour they are supposed to represent. This has been proved by F. B. Power and V. K. Chesnut[3] in their recent investigation of the odorous constituents of peaches. The authors used for their experiments the fresh pulp of selected ripe fruits (Georgia Belle), carefully deprived of the pits. This material was subjected to distillation in various quantities (106.6, 108.4, 120.2 and 14.18 kos.), but each time in one operation and without any added water, in a current of steam. The amount of distillate collected was about 65 liters in the three first cases and 12 liters in the last test. This liquid was repeatedly cohobated until the odorous substances were concentrated in volumes of 4.2, 2, 2 and 0.5 liters, respectively. From one such concentrated distillate the authors obtained by repeated extraction with ether 0.00074 per cent. of essential oil. In another case, when 155.6 kilos of peaches were distilled and the whole distillate extracted with ether, the yield of essential oil was 1.2774 grams = 0.00082 per cent. The oil obtained was limpid, pale yellow and possessed an exceedingly fragrant, intense peach-like odour. When cooled somewhat below the ordinary temperature, it formed a concrete transparent mass, which was interspersed with small acicular crystals, the latter evidently consisting of a paraffin hydrocarbon, melting at 52°. The essential oil from peaches is very unstable. When exposed to the air, it becomes converted into a black, viscid mass and loses completely its original fragrance. Only when kept in a hermetically sealed glass tube, it appeared to remain unchanged. The oil probably consisted in the main of the linalyl esters of formic, acetic, valeric and caprylic acids, together with a little acetaldehyde and furfural, the latter having doubtless been produced during the process of distillation by the action of the organic acids on the sugar contained in the fruit. The presence of cadinene, or a compound giving a similar colour reaction (red colouring with glacial acetic and concentrated sulphuric acids), was also indicated.

In order to prove the presence of linalool, the authors saponified 2 litres of the concentrated distillate with 25 grams of pure sodium hydroxide and distilled the saponified liquid, collecting about 800 cc. of the distillate. By extraction of this liquid, which smelled of linalool, with ether, 0.2620 grams = 0.00024 per cent. of a yellowish, oily residue were obtained, containing a small amount of solid substance, probably a hydrocarbon. Oxidation of the oily residue (linalool) lead in the end to a yellowish

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[1] Comp. also Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. III, p. 571. — [2] *Bull. Imp. Inst.* 18 (1920), 346. — [3] *Journ. Americ. chem. Soc.* 43 (1921), 1725.

oil, which had the pronounced odour of citral. On the addition of Schiff's reagent, it soon developed a purplish colour and it rapidly reduced an ammoniacal solution of silver oxide. A further identification of the citral and, consequently, the linalool, was not possible, the available quantities being too small.

The authors proved further that the saponified distillate, extracted with ether, contained very small quantities of methyl alcohol (oxidation with potassium permanganate led to formaldehyde). The acids were characterized by their silver salts; the aldehydes (acetaldehyde and an aldehyde of higher molecular weight) were prepared from the bisulphite compounds.

In a similar way as in their investigation of the odorous constituents of apples[1], the authors proved that the aromatic substances of peaches contain traces of acetaldehyde, even if prepared without the assistance of heat.

No trace of hydrocyanic acid or benzaldehyde could be detected in the distillate from peach pulp. It may therefore be concluded that amygdalin is restricted to the kernels of the fruit.

Peppermint Oil, American.—Although the use of American peppermint oil is almost out of the question now in Germany, owing to tremendous rate of exchange for the dollar, we were nevertheless able to purchase small quantities of our well-known brand "F. S. & Co.", as abroad; especially in the neutral countries, there are a good many customers for it, who only reluctantly would use another quality instead. Under the influence of the large stocks from 1920 and the general depression in the United States, last year's price of $ 5.75 per pound of good crude oil was no longer to be maintained. The market gave way quickly, especially after the 1921 crop had shown the splendid result of 350 000 lbs., so that it was possible in the end to buy at $ 1.50. This figure attracts the attention of the speculators and it is the talk already now that producers and dealers, who already last winter tried everything in order to prevent the article from declining any further, will not allow the control of the stocks to pass out of their hands. The quantities available were rather important towards the end of 1921 and as the 1922 crop will very probably also give a good result, one may reckon with a continuance of the present low prices, at least for the near future. Besides, a considerable enlargement of the peppermint fields in the West is to be expected, as other agricultural products promise still less benefit for the time being. The absence of the regular German demand makes itself keenly felt, of course, but as long as France and England do everything in order to damage our political economy and to reduce the buying power of our money, it is not to be thought of a recurrence of the former export of American peppermint oil to Germany.

The fiftieth anniversary of the day of their firm's foundation (August 28th, 1871) has induced our New York friends, Messrs Fritzsche Brothers, Inc., to ask their representative in the peppermint districts for an extensive historical report covering the period of 50 years. It contains a good many important data concerning the development of the peppermint oil industry in the United States and we copy some of the details which might interest our readers.

The cultivation of peppermint in the West started as far back as 1852 to 1854, in the County of St. Joseph in Michigan. The distillation took place especially in the towns of Florence, Sherman, and Lockport. In the years from 1858 to 1860, there were about 10 farmers who grew peppermint, each about 30 to 50 acres of hilly land. The

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[1] Comp. *Bericht* (German) 1921, 7.

yield was then from 25 to 30 lbs. of oil in the first, 18 to 20 in the second and 12 to 15 in the third year. The prices ranged in 1852 to 1854 between $ 2.50 and $ 3.50 per lb., the total production being perhaps about 25000 lbs. per year. The system of distillation differed little from the present one, only that then the stills were smaller. Up to 1860 the chief district for peppermint was Wayne County in the State of New York, but later on the importance of the Michigan peppermint fields grew rapidly. Towards the end of the seventies, one started there the cultivation in lower, well-watered districts (marshes) which were easier to work and keep free from weeds. Little by little, the Michigan growers acquired a monopoly, as their costs of production were lower than those of their colleagues in the State of New York. English peppermint plants were first introdued in 1892 and cultivated in thee neighbourhood of Nottaway in the County of St. Joseph. This proved to be a complete success, as the English plants are more hardy than the American ones and yield almost twice the quantity of oil. After a short while, the American plants had been replaced almost completely by the English ones, and only in the neighbourhood of Charlotte in the State of Michigan, there are still some plantations of the pure American variety. The bad yield in oil indicates at once where both varieties are mixed. The cultivation of peppermint in Wayne County (New York) has ceased altogether.

According to Magnus, Mabee and Reynard, Inc.[1]) the peppermint oil of the last crop shows an exceptional rotatory power (α_{D20° —17 instead of —23°) and contains but little menthol.

E. R. Kremers[2]) obtained by cohobation of the watery distillate of American *Mentha piperita* three fractions of the following properties:— d_{24° 0.916 to 0.940, n_{D24° 1.468 to 1.476, ester v. 21.65 to 29.9, ester content 7.7 to 10.6 per cent., alcohol as ester 6.0 to 8.3 per cent., ester v. after acetylation 195 to 160.5, total alcohol 63.6 to 50.8, free alcohol 57.6 to 42.5 per cent. The chief components were menthol (preparation of pure menthol, without any indication of the constants) and menthone (semicarbazone, m. p. 185°. Menthyl ester and 1,3-methylcyclohexanone (b. p. 169°, d_{21° 0.915, n_D 1.4430, semicarbazone, m. p. 180°) were present in small quantities.

As to the history of peppermint oil in America, see page 105 of this *Report*.

Peppermint Oil, Italian.—G. Micheletti[3]) communicates that this year's peppermint crop in Italy (Vigone, Pancalieri, Piemonte) is satisfactory. 30000 kilos of oil were obtained, a quantity superior to last year's result. The quality was also better. The menthol content exceeded 50 per cent. on an average.

Peppermint Oil, Japanese.—The lack of demand, characteristic of the Japanese peppermint market during the first months of the year covered by this *Report*, would certainly have lead to a reduction of the prices in the course of the summer, if not speculators had done everything to hold them and even send them up, if possible, by means of extensive advances of money granted by the banks. They succeeded in bringing about a temporary firmness of the market in autumn, but under the influence of the new crop and the considerable old stocks the opinion seems to prevail in the quarters concerned that a fall of the prices is not improbable in the near future, unless unforeseen events prevent it. The stocks in Japan about the middle of February

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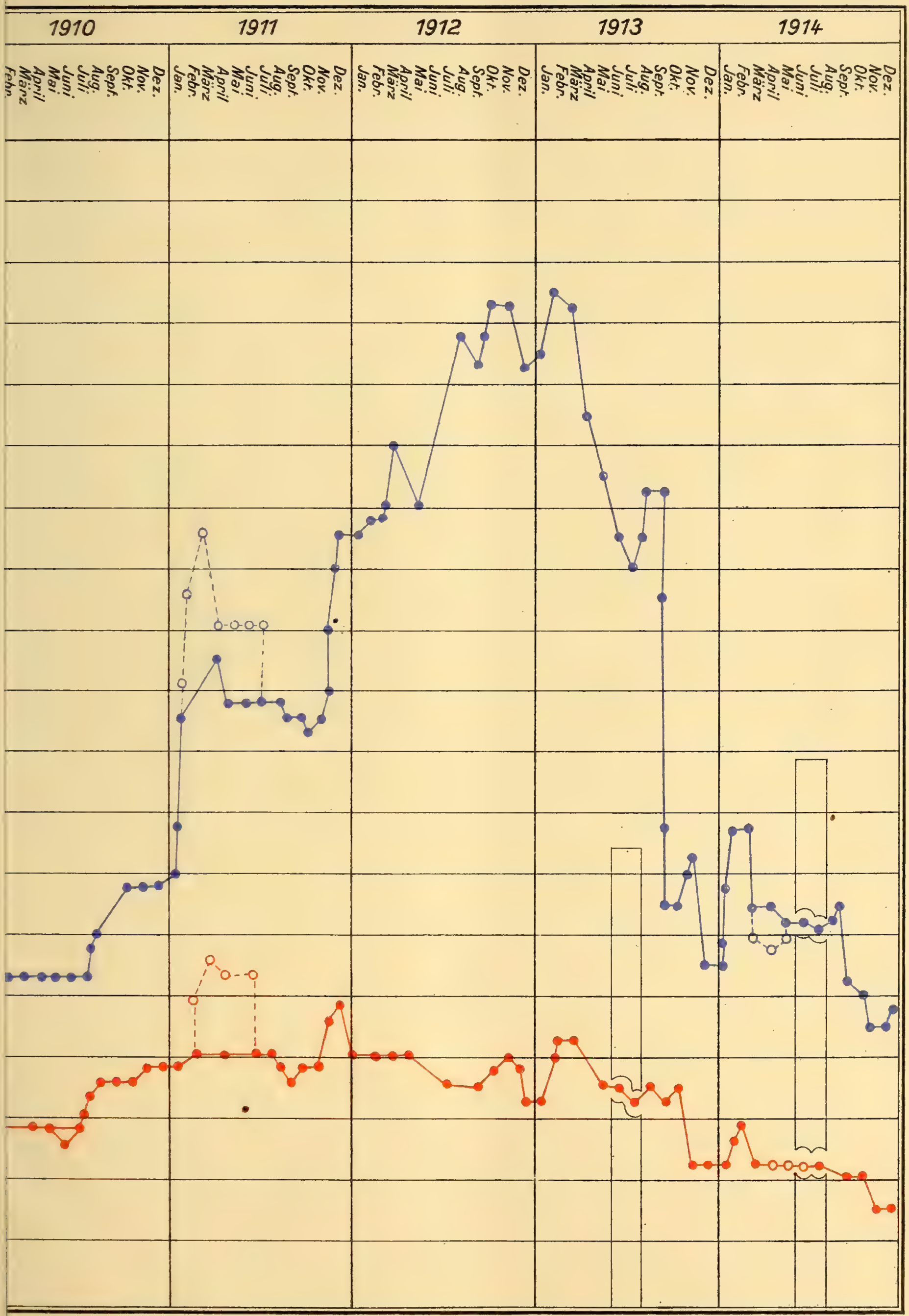
[1]) *Oil, Paint and Drug Reporter* **100** (1921) Nº 17, 31. — [2]) *Journ. Americ. Pharm. Assoc.* **10** (1921), 835. — [3]) *Parfum. moderne* **14** (1921), 215.

Distillation of Peppermint Oil in Japan.

(After a water-colour painting in the possession of the Perfumery Department of the German Museum in Munich. Gift of the firm of Schimmel & Co.)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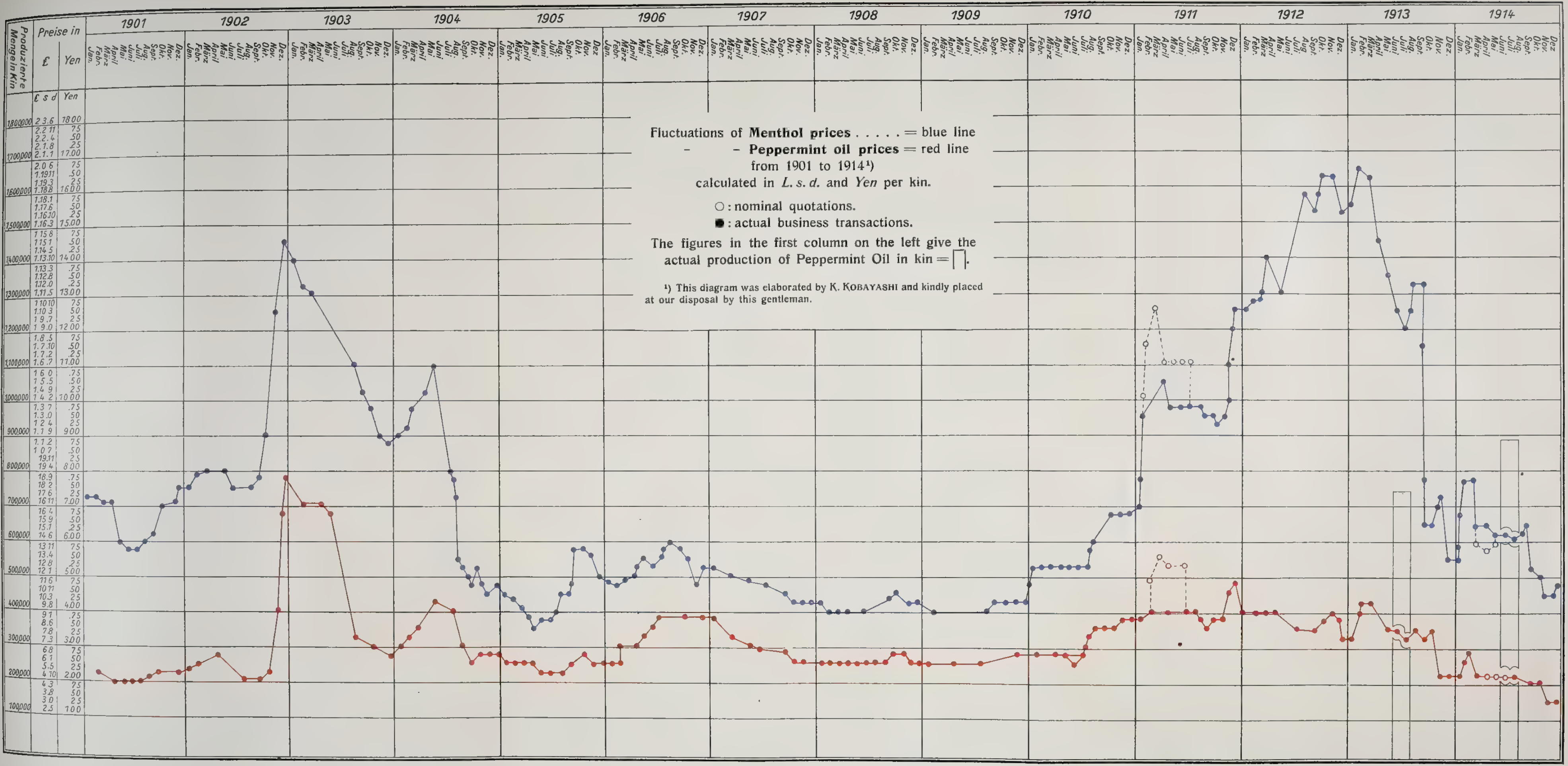
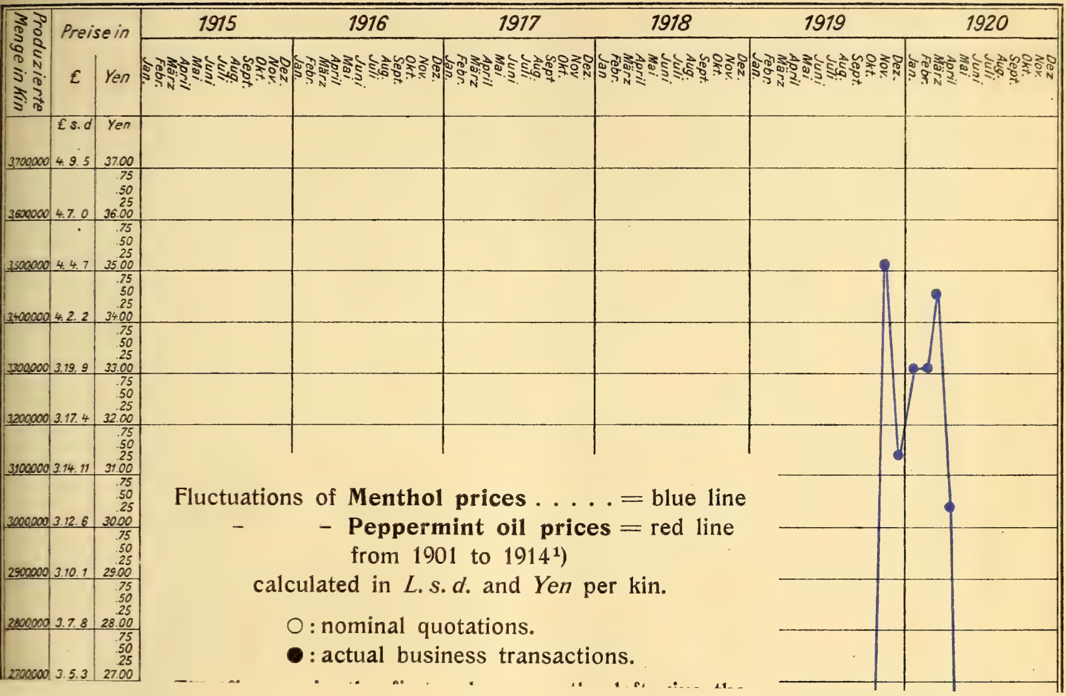


Fluctuations of **Menthol prices** . . . . . = blue line
– – **Peppermint oil prices** = red line
from 1901 to 1914[1])
calculated in *L. s. d.* and *Yen* per kin.

○ : nominal quotations.
● : actual business transactions.

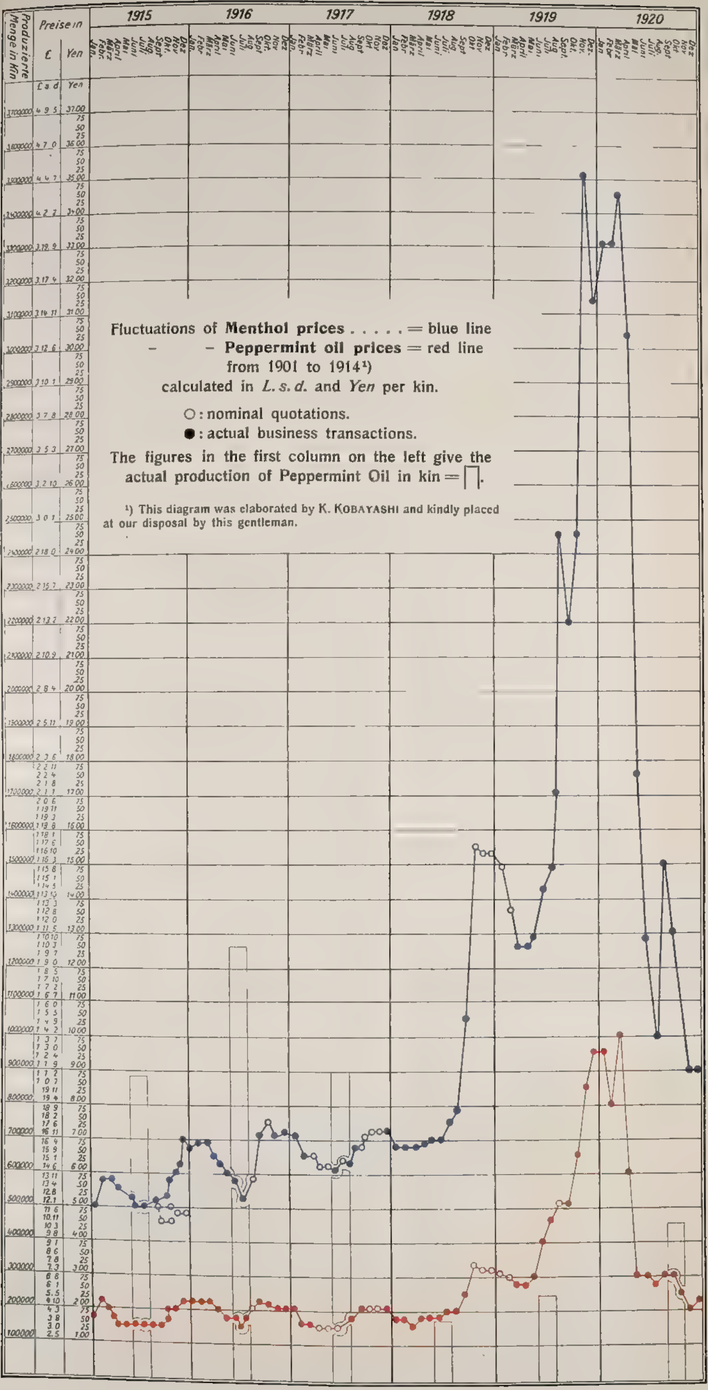
The figures in the first column on the left give the actual production of Peppermint Oil in kin = ▯.

[1]) This diagram was elaborated by K. KOBAYASHI and kindly placed at our disposal by this gentleman.



Fluctuations of **Menthol prices** . . . . . = blue line
– – **Peppermint oil prices** = red line
from 1901 to 1914¹)
calculated in *L. s. d.* and *Yen* per kin.

○ : nominal quotations.
● : actual business transactions.



Fluctuations of **Menthol prices** . . . . . = blue line
– – **Peppermint oil prices** = red line
from 1901 to 1914[1])
calculated in *L. s. d.* and *Yen* per kin.

○ : nominal quotations.
● : actual business transactions.

The figures in the first column on the left give the actual production of Peppermint Oil in kin = ⊓.

[1]) This diagram was elaborated by K. KOBAYASHI and kindly placed at our disposal by this gentleman.

are said to have been 6200 cases of menthol and 7100 cases of peppermint oil, so that it seems to be only a question of time when the holders will come down with their prices, in order to revive the demand. The Japanese refiners also keep back with their purchases of crude oil, limiting themselves, as it seems, to satisfy what little demand there may be out of their old stocks. The quantities mentioned above represent about 700000 lbs. of oil, to which the rather considerable stocks in London, New York and Hamburg have to be added. It has generally been possible of late to buy much cheaper in London than in the producing country.

The Japanese export statistics, rectified of late, give the following figures for the last 13 years:—

	Peppermint Oil		Menthol	
1909	151 800 kin to the value of Yen	466 600	102 400 kin to the value of Yen	490 500
1910	146 200 „ „ „ „ „ „	464 500	116 900 „ „ „ „ „ „	648 800
1911	172 400 „ „ „ „ „ „	625 600	113 600 „ „ „ „ „ „	963 200
1912	184 900 „ „ „ „ „ „	699 300	133 200 „ „ „ „ „ „	1 589 700
1913	282 100 „ „ „ „ „ „	1 017 700	232 900 „ „ „ „ „ „	2 872 800
1914	277 760 „ „ „ „ „ „	818 800	269 300 „ „ „ „ „ „	1 816 100
1915	341 200 „ „ „ „ „ „	697 400	323 500 „ „ „ „ „ „	1 851 000
1916	360 700 „ „ „ „ „ „	844 500	386 500 „ „ „ „ „ „	2 410 600
1917	259 700 „ „ „ „ „ „	593 600	251 200 „ „ „ „ „ „	1 594 300
1918	214 700 „ „ „ „ „ „	539 700	237 500 „ „ „ „ „ „	1 554 000
1919	409 199 „ „ „ „ „ „	1 307 113	239 973 „ „ „ „ „ „	2 546 898
1920	321 300 „ „ „ „ „ „	1 848 000	363 400 „ „ „ „ „ „	5 417 000
1921	245 400 „ „ „ „ „ „	558 413	229 900 „ „ „ „ „ „	2 172 480

The diagram here inserted has been sketched and kindly placed at our disposal by Mr. K. Kobayashi. It gives an idea of the prices paid for menthol and peppermint oil in the years from 1901 to 1920. The blue dots represent the menthol, the red ones, the peppermint oil; "o" means nominal quotation, no business having been done at the figure, whereas in the cases marked "●" actual sales resulted.

Specially striking in the diagram are the periodical rises of the quotations for peppermint oil in the years 1902/03, 1912/13 and 1919/1920, which did not last very long, however. Whereas the high prices of 1902/03 were due to precipitated purchases of the American Government[1]), those of 1912/13 to the bad crop[2]), the last quite extraordinary rise can only be looked upon as a consequence of the war.

R. E. Kremers[3]) investigated the oil obtained through cohobation of the distillation water of the Japanese peppermint. It had the following properties:—d_{18° 0.938, n_{D18° 1.485, ester v. 39.2, ester v. after acetylation 69.1, ester content 13.8 per cent., alcohol as ester 10.9, total alcohol 20.3, free alcohol 9.4 per cent. It was impossible to establish the presence of menthol, whereas the fractionated distillation yielded a product composed almost entirely of pulegone (nitroso derivative, m. p. 83°, semicarbazone, m. p. 167°).

Pimento Leaf Oil.—On page 76 of our last *Bericht* (German), we quoted a communication from an English source, according to which it was possible to obtain 100000 lbs. of pimento leaf oil annually in Jamaica. The original paper[4]) now before

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[1]) Comp. *Report* April **1903**, 60. — [2]) *Ibid.* April **1912**, 99. — [3]) *Journ. Americ. Pharm. Assoc.* **10** (1921), 834. Comp. also the water oil of the American peppermint and of *Monarda fistulosa*, pages 58 and 50 of this *Report*. — [4]) *Commerce Reports*, N° 257 of November 1st, **1920**.

us states that the trials of preparing oil from the leaves are still going on in the Government Laboratories of Jamaica. The production on a large scale was not yet possible. It is further said that experiments had shown the pimento leaf oil to contain 1.8 per cent. eugenol, from which it would be possible to prepare to advantage *iso*eugenol and vanillin.

Pine Needle Oils.— A comparative investigation of Eastern and Western hemlock oils has been started by D. E. Cable1). Five oils originating from the East (Michigan, Wisconsin, New Hampshire, Tennessee, Virginia) which were distilled during the months of June, July, and August from the stripped leaves of *Tsuga canadensis*, Carr. with a yield of 0.29 to 0.65 per cent., showed the constants:— $d_{15^\circ}^{20^\circ}$ 0.9020 to 0.9234, $[\alpha]_{D20^\circ}$ — 14.80 to — 21.65°, n_{D20° 1.4691 to 1.4704, acid v. 0.33 to 0.70, ester v. 103.8 to 147.35, ester v. after acet. 113.5 to 171.94, esters calc. as bornyl acetate 36.33 to 51.57 per cent., total borneol 31.24 to 47.41. The Wisconsin oil excelled by its high content of esters and of total borneol.

Three oils from Western hemlock, originating from Coeur d'Alene, Idaho, behaved quite differently. They were distilled in the months of May, June, and July 1920 from the stripped leaves of *Tsuga heterophylla*, Sargent (yield 0.32 to 0.36 per cent.) and showed the constants as follow:— $d_{15^\circ}^{20^\circ}$ 0.8444 to 0.8521, $[\alpha]_{D20^\circ}$ — 6.74 to — 20.00°, n_{D20° 1.4790 to 1.4840, acid v. 2.57 to 3.4, ester v. 6.7 to 17.25, ester v. after acet. 19.6 to 33.4, esters calc. as bornyl acetate 2.35 to 6.02 per cent., total borneol 5.43 to 9.24 per cent.

For the purpose of comparing these oils with ordinary commercial hemlock oils of the years 1909 and 1919, the following constants for three oils of commerce were ascertained:— $d_{15^\circ}^{20^\circ}$ 0.9190 to 0.9664, $[\alpha]_{D20^\circ}$ — 14.85 to — 24.85°, n_{D20° 1.4721 to 1.4786, acid v. 1.51 to 18.45, ester v. 105.09 to 115.41, ester v. after acet. 149.51 to 150.83, esters calc. as bornyl acetate 36.78 to 40.39 per cent., total borneol 41.55 to 41.74 per cent.

The last-named oils are remarkable on account of the extraordinary high upper values for density, refractive index, and acid content indicating, partially, resinification.

The essential oil of the needles from *Pinus silvestris*, L. of Russian origin has hitherto been investigated only by Hirschsohn2) and, later on, by J. Schindelmeiser3). According to this author, Russian pine needle oil constitutes an oil with a pleasant aromatic odour, showing the constants:— b. p. 160 to 250°, d_{18° 0.875, $\alpha \pm 0$. On fractionated distillation from 10 to 10° the following fractions resulted:— 160 to 170°, 48 per cent.; 170 to 180°, 32 per cent; 180 to 190°, 12 per cent. The first fraction was optically active ($\alpha_D + 2^\circ 30'$) and contained *d*-pinene; nitrolamine, m. p. 118°. The fraction 170 to 180° was lævorotatory ($\alpha_D - 2^\circ 46'$) and contained, in the opinion of the author, equally as the fraction 180 to 190°, *l*-limonene in addition to some *d*-limonene (tetrabromide of the total limonene, m. p. 125 to 126°, dihydrobromide of the total limonene, m. p. 64°; cf. the constants of the corresponding dipentene derivatives). The fraction boiling above 190° contained inactive borneol (phenylurethane, m. p. 137 to 138°) and, probably, some cadinene (dihydrochloride, m. p. 117 to 118°). Hence, the oil resembled in its composition, apart from the absence of sylvestrene, the German and the Swedish pine needle oils4).

Quitch Root Oil.— It is little known that quitch root (*Triticum repens*, L.) contains an essential oil. A trial distillation of selected roots from Miltitz fields yielded

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1) *Journ. Americ. pharm. Assoc.* 10 (1921), 170. — 2) *Pharm. Zeitschr. f. Russland* 481 (1891). — 3) *Sitz.-Ber. d. Naturforscher-Ges. b. d. Universität Jurjew (Dorpat)* 13, 2 (1903), 315. — 4) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, p. 122 and *Bericht* (German) 1920, 35.

0.0065 per cent. of a dark brown distillate of feebly aromatic, somewhat sweetish odour; d_{16° 0.9665, acid v. 36.2, ester v. 29.0, incompletely soluble in 10 vols. of 80 per cent. alcohol. Rotation and refraction could not be determined on account of the dark colour of the oil.

Another batch of quitch roots, mixed with tarragon roots, however, yielded 0.052 per cent. of essential oil of light brown colour: — d_{15° 0.9670, $\alpha_D + 2^\circ 30'$, n_{D20° 1.55359, acid v. 5.4, ester v. 10.6, incompletely soluble in 10 vols. of 80 per cent. alcohol, soluble in 2 vols. and more of 90 per cent. alcohol.

Ravensara Oil. — The leaves and young twigs of *Ravensara aromatica*, J. F. Gmel., a lauracea growing on the high plains of Madagascar, yielded on distillation with steam an essential oil of an agreeable, camphor-like smell. It reminded one of eucalyptus oil and consisted, according to Ferrand and Bonafous[1]), of a terpene mixed with an oxygenated body.

Roman Chamomile Oil. — According to Massera[2]), the oil contained in the flowers of Roman chamomiles to the extent of 0.8 to 1 per cent. had the following constants: — d 0.905 to 0.920, $[\alpha]_D - 3^\circ$ to $+ 3^\circ$, sap. v. 220 to 320, soluble in less than 1 vol. and, with slight turbidity, in 3 vols. of 70 per cent. alcohol. In addition to the components enumerated by the author (*iso*butyl and *iso*amyl esters of angelic and tiglic acid, anthemol and anthemene), azulene is present, besides, according to Blaise, *n*-butylic alcohol and, according to van Romburgh, also β-methylethylpropylic alcohol[3]).

Rose Oil, Bulgarian. — The estimations of the 1921 crop vary between 1200 and 1500 kilos. Although these quantities do not come up by for the average pre-war results, they are about 20 per cent. better than last year's result. This excess has not had any effect on the prices, however, and the market remained almost unaltered. It was remarkable to what an extent the illegitimate trade with rose oil has grown. It is understandable that the important banks are greatly interested in transactions concerning such a valuable commodity and that even the State may now and then sell certain important lots, last year, however, rose oil was offered from many other quarters, which have but little or nothing at all to do with the distillation of otto of roses. The number of such sellers, who often carried their goods about with them in handbags, was specially large, among them a good many Bulgarian students, who meant to earn like that the means necessary for continuing their studies at German universities. It is desirable that these after-effects of the war should disappear quickly, to the benefit of the legitimate trade. Many a buyer who was not in a position to test the "bargain" offered, has been done in such transactions.

T. H. Shipkoff[4]) publishes an article on the Bulgarian rose industry, from which we copy some data, as far as they are not contained in our previous *Reports*[5]). The district in Bulgaria, called by all western travellers "The Land of the Roses", extends over that portion of the southern slopes of the main Balkans mountains, which comprises the whole branch range of Stredna Gora (Little Balkans). Its average length is about 80 miles and its average with about 30 miles[6]). The average elevation of the rose district is bout 1300 feet above the level of the sea, and the average height of the

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[1]) *Parfum. moderne* **14** (1921), 100. — [2]) *Rev. Ital. d. Essenze e Profum.* As per *Perfum. Record* **12** (1921), 283. — [3]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. III, p. 616. — [4]) *Americ. Perfumer* **16** (1921), 48. — [5]) Comp. *Reports* April **1908**, 86; April **1913**, 89; **1916**, 47. — [6]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, p. 552, map.

main Balkans in the north is about 5600 feet, while the average height of the Little Balkans is about 3700 feet. There are over 180 communities or villages with more than 21000 small proprietors of rose gardens owning on an average about one acre each. Only about half of the 14000 small native stills, existing in the country, are still in use, for during the last years before the great war, 12 modern distilling plants have been built.

Whereas this industry had developed steadily up to the Balkan war in 1912, it decreased continuously from that time. The consequences of the hard years of war are still felt and other agricultural products have taken the place of the roses, although the demand for otto of roses has trebled of late. From 1889 to 1912 the area planted with roses increased from 7500 to 30000 acres, yielding on an average up to 27000000 lbs. of roses, from which 3600 to 4000 kilos of rose oil were obtained. The record crops of 1900 and 1907 yielded even 30000000 lbs. of flowers each, or about 175000 ounces of otto of roses.

The present area cultivated with roses will hardly exceed 14000 acres and the yield of oil has also gone down, as the rose gardens have been neglected and not sufficiently manured. The quantity of oil produced went down from 4000 kilos in 1912 to 2410 kilos in 1917, 1840 in 1918, 1600 in 1919, 1200 in 1920[1] and for 1921 only 1000 kilos are expected.

Prior to the war, the exports were as follows: —

Destination	1900	1906	1911
France	1548 kilos	2607 kilos	1483 kilos
United States . . .	849 „	1524 „	525 „
Germany	568 „	1113 „	1595 „
Great Britain	1175 „	1074 „	572 „
Russia	202 „	278 „	158 „

During the war, nothing was exported to the United States, France, England and Russia, whereas Germany imported annually 1700 kilos, Switzerland about 600 kilos, Austria about 200 kilos, together with Holland. Since the war is over, the American market has been the most important by far. In 1919, 3500 kilos were exported to the United States, 900 kilos to France and 400 kilos to England[2]. The exports to Germany are supposed to have risen considerably in 1920.

Rosemary Oil. — On Spanish oil of rosemary, see page 106 of this *Report*.

Sandalwood Oil, East Indian. — The Department of Statistics in India publishes the following statement showing the exports of sandalwood oil[3]: —

	January 1921		Ten months, April 1920 to January 1921.	
Countries of final destination	Quantity	Value	Quantity	Value
Great Britain	6237 lbs.	155925 Rs.	109652 lbs.	2745600 Rs.
France	2930 „	69000 „	5030 „	125000 „
Straits Settlements . . .	—	—	190 „	2300 „
Ceylon	—	—	4 „	275 „
Hong Kong	720 „	4320 „	1290 „	8880 „
Asiatic Turkey	—	—	—	15 „
Java	—	—	980 „	20300 „
Portuguese East Africa .	—	—	2 „	40 „
Egypt	—	—	1190 „	32825 „
Australia	—	—	100 „	2150 „
Total	9887 lbs.	229245 Rs.	118438 lbs.	2937385 Rs.

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[1] It is stated officially that the 1920 crop yielded only 900 kilos, comp. *Bericht* (German) 1921, 39. — [2] These figures, compared with those given for the actual production of rose oil, confirm the well-known fact that Bulgarian Otto of Roses is exported only with the usual addition of palmarosa oil. — [3] *Perfum. Record* 12 (1921), 180.

In the report on the Administration of Mysore1) for the year ending June last, it is stated that the sandalwood oil factories dealt with 1362 tons of sandalwood. The demand for the oil was good, but the profits were small, as the prices of the wood had been driven up very high in the Coorg and Madras auctions.

As the Dutch East Indies export sandalwood and on the other hand import about 1000 lbs. of sandalwood oil annually from British India, the Government intends to produce it in the country. A question still to be solved would be the cutting of the wood into chips, in which direction experiments are going to be made. Out of 37 kilos of sandalwood 1023 cc. = 2.6 per cent. of oil have been distilled2). The plan seems to have come to nothing, however, for according to a report of the Dutch Chamber of Commerce in New York3) the distillation of sandalwood oil in Java, begun during the war, has been given up again, as being unprofitable.

E. J. Parry4) communicates that during the last years he frequently received from reliable French or English (Indian) distillers sandalwood oils which were fit for use in perfumery but the constants of which did not comply with the requirements of the British Pharmacopeia. In his opinion, the distillation in such cases had either been incomplete or too slow. Parry proves experimentally that a prolonged action of steam on the oil altered the constants, reducing in particular the optical rotation.

We would add that this is nothing new, for we have pointed out years ago5) that the decomposition products, which easily form during the distillation, alter the properties of the oils and that only a very careful distillation will yield a normal product.

Sandalwood Oil, West Indian. — Large quantities of wood have arrived of late and we hope to be able before long to supply fresh oil on a larger scale.

Oil of Satureia montana. — By steam-distillation of the not yet flowering dry herb of *Satureia montana*, L., gathered in June in the Italian province of Aquila, P. Leone and E. Angelescu6) obtained 0.69 per cent. of a yellow of strong aromatic smell and burning taste. By extraction of the herb with acetone and distillation of the extract with steam, the authors obtained 1.63 per cent. of an oil which had the same specific gravity and the same phenol content as the former. It is to be supposed, in consequence, that the dry herb contains in realty at least 1.63 per cent. of oil. — The oil had the following properties: — $d^{25°}_{4°}$ 0.9053, $[\alpha]_{D17°}$ — 3.05°, $n_{D16°}$ 1.49926, acid v. 2.22, sap. v. 6.75, ester v. 4.53, corresponding to an ester content of 1.58 per cent. (calculated as linalyl acetate), carvacrol content 28 per cent. (nitroderivative, m. p. 77 to 78°; determined through shaking with a 5 per cent. soda lye). The oil freed from the phenol contained 10 per cent. of an alcohol, which has not been identified more closely (sap. v. after acet. 54.3) and yielded the following fractions on repeated distillation under normal pressure: — 1. b. p. 170 to 180° (54 per cent.), 2. b. p. 180 to 190° (12 per cent., 3. b. p. 190 to 205° (8 per cent.), 4. b. p. 205 to 232° (6 per cent.), 5. b. p. 232 to 252° (12 per cent.). After having been boiled for five hours with metallic sodium, the first and second fractions yielded other fractions boiling at 173 to 175° (38.1 per cent.) and at 176 to 178° (20.3 per cent.), consisting of cymene (hydroxy*iso*propylbenzoic acid, m. p. 156 to 157°) and dipentene

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1) *Americ. Perfumer* **16** (1921), 107. — 2) *Chemist and Druggist* **94** (1921), 406. — 3) *Holland and her colonies* **1** (1921), No. 7, p. 15. — 4) *Parfum. moderne* **14** (1921), 54. — 5) Comp. *Report* April **1908**, 92. — 6) *Gazz. chim. ital.* **51** (1921), II. 368.

(nitrolbenzylamine, m. p. 108°), respectively. The original oil, therefore, contained abou 27 per cent. of cymene and 14 per cent. of dipentene.

The oil of the French plant has been investigated already years ago by several authors. A. Haller found in it 35 to 40 per cent. of carvacrol. According to our determinations an oil from Barrême contained about 27 per cent. and one from Sault about 32 per cent. of carvacrol[1].

Oil of Skimmia laureola. — The oil of *Skimmia laureola*, Hook. fil., on whose origin and properties we gave a short notice p. 46 on of our last *Bericht* (German ed.), has recently been investigated by J. L. Simonsen[2]. On distilling the shade-dried leaves collected in the Chakrata Division during June and early July, the author obtained about 0.5 per cent of a pale emerald-green oil with the following constants: $d_{30^\circ}^{30^\circ}$ 0.9041; n_{D30° 1.4648; acid v., 3.63; sap. v. 197.36; sap. v. after acet. 238.6 (prior to acetylation the oil was mixed with turpentine oil)[3]. After washing the oil with dilute alkali, the oil was repeatedly fractionated under 200 mm. pressure and the following fractions were obtained: — 1. B. p. 130 to 140°, 0.46 per cent.; 2. 140 to 145°, 4.6 per cent.; 3. 145 to 150°, 0.61 per cent.; 4. 150 to 155°, 8.4 per cent.; 5. 155 to 160°, 2.3 per cent.; 6. 160 to 167°, 2.0 per cent.; 7. 167 to 173°, 50 per cent.; 8. 173 to 177°, 0.61 per cent.; 9. 177 to 182°, 1.05 per cent.; 10. 182 to 190°, 1.2 per cent.; 11. above 190°, 18,2 per cent.

The first three fractions contained a hydrocarbon boiling at 130 to 135° (200 mm.) or 176 to 182° (695 mm.); $d_{30^\circ}^{30^\circ}$ 0.859; $[\alpha]_{D30^\circ}$ — 4.11°; n_{D30° 1.471), the nature of which remained undecided. Fraction 4 consisted of nearly pure *l*-linalool (phenylurethane, m. p. 65°). The fractions 5 to 9 contained partly *l*-linalool, partly *l*-linalyl acetate, partly a mixture of both. In addition, fractions 8 to 10 contained a high-boiling alcohol. From fraction 11, repeated distillation yielded unpleasently-smelling oils, possibly mixtures of sesquiterpene alcohols and esters.

Hence, the oil investigated consisted in the main of *l*-linalyl acetate, furthermore of *l*-linalool, a hydrocarbon and a mixture of sesquiterpene alcohols and esters.

Spearmint Oil. A sample of the entire dried plant of *Mentha longifolia* (Host, or Huds.?) collected in the Somerset East district of the Cape Province and consisting of leaves 40 p. c., and loose stalks 60 p. c., was examined at the Imperial Institute[4]. The stalks were found to be practically free from volatile oil, the leaves yielded on steam distillation 2.4 per cent. oil, equivalent to a yield of 0.98 per cent. from the entire original sample. The colourless oil had the characteristic odour and taste of spearmint oil and the following constants:—$d_{15^\circ}^{15^\circ}$ 0.947; α_D — 47.6°; n_D 1.4925; ketones (estimated by sulphite method), calculated as carone, 70 per cent. The oil from this sample of spearmint resembled the oils from *Mentha spicata*, Huds. and of *Mentha viridis*, L., but contained a very high percentage of ketones and corresponded in this respect with the Austrian spearmint oil.

Spike Oil. — As to Spanish spike oil, see page 106 of this *Report*.

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[1] Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. III, p. 470. — [2] *Journ. Soc. chem. Ind.* **40** (1921), T. 126. — [3] The above constants differ considerably from those found by Roure-Bertrand Fils (comp. *Bericht* **1921**, p. 46). With a leaf oil forwarded to us we ascertained the following characters: — d_{15° 0.8876, $\alpha_D + 2^\circ 22'$, n_{D20° 1.47260, acid v., 0, sap. v., 128.8 = 45.1 per cent. of esters, calculated as linalyl acetate; soluble in 0.2 vol. 90 per cent. alcohol, with more than 1.3 vol. strong opalescence. The colourless oil showed a bluish fluorescence and recalled the odour of petitgrain oil. It was said to originate from *Skimmia laureola*, Sieb. et Zucc. (*Limonia laureola*, D.C.), Roure-Bertrand Fils state *Skimmia laureola*, Hook. fil., which name we fail to find in the *Kew Index*. — [4] *Bull. Imp. Inst.* 18 (1921), 350.

Distillation of Essential Oils in Spain.

Staranise Oil. — The following statistics of maximum and minimum prices of staranise oil are taken from an English periodical[1]: —

	Maximum	Minimum		Maximum	Minimum
1911	6/0	4/9	1916	3/6	3/2
1912	6/11	5/6	1917	4/6	3/3
1913	7/3	6/3	1918	6/2	4/0
1914	6/3	5/0	1919	6/0	4/2
1915	4/9	3/0	1920	6/0	3/6

As it is shown, the maximum pre-war prices have not been reached again, in spite of the universal depreciation of the money. Although in November 1921 the price went down as far as 2/2 per lb.[2]), it was believed that this was not the lowest yet, for there were considerable stocks and little demand. In 1921, 4000 cases of $66^{2}/_{3}$ lbs. each arrived in London, where abundant stocks existed already. The oil was imported partly in exchange for textiles.

It is further stated that formerly there was a good market for staranise oil, chiefly for liqueurs and confectionery. Nowadays the Russian demand is missing and France, Germany and the United States require but little. In the latter country, the decrease in the demand for staranise oil is ascribed to the prohibition of alcoholic drinks. The best consumers of the articles are now most likely Spain and South America, but it is expected that the French and English demand will increase again.

Oil of Tagetes anisata. — The fresh herb of *Tagetes anisata,* Lillo, *n. sp.,* a composita growing in the pampas of Argentina at an elevation of from 1000 to 3000 m., yielded on steam distillation, according to F. Zelada[3] 0.7 to 0.8 per cent. of a green oil. The product resembled anise oil and had the following properties: b. p. 214 to 218°, solidification p. — 6°, d_{15° 0.9862, α — 1°10′, n 1.5432, ester v. after acetylation 23.4, sap. v. 3.1, iodine v. 158.5, alcohol as $C_{16}H_{18}O$ 0.852 per cent., ester as $C_{16}H_{17}OCOCH_3$ 1.082 per cent., total alcohol as $C_{16}H_{18}O$ 3.229 per cent., soluble in 5 vols. of 90 per cent. alcohol[4].

Tarragon Root Oil. — See Estragon root oil, p. 34 of this *Report.*

Thyme Oil. — The Spanish oils of thyme are of different composition and may be grouped in oils containing thymol, carvacrol, or citral. The same division could be used for the manifold species of *Thymus* occurring in Spain. According to the few existing authentical indications concerning the botanical origin of the Spanish thyme oils, there seems to be a certain conformity in the characteristics of the plants belonging to one and the same of the groups mentioned. According to Rubeck and E. H. Holmes[5], *Thymus vulgaris,* L., and *Thymus Zygis,* L., which are much alike and are both known in Spain by the name of *tomillo salsero,* being used as pot-herbs, certainly belong to the first group. *Thymus hyemalis,* Lange, according to Holmes the mother-plant of the so-called Spanish verbena oil, is closely allied to *Thymus hirtus,* Willd. *(tomillo limonero):* both kinds contain citral[6]. The similarity appears to be less striking (the relative indications in books, etc. are very scanty) between *Thymus Mastichina,* L., *(tomillo blanco)* and *Thymus cephalotus,* L., the oils of which according to Dorronsoro[7]

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[1] *Chemist and Druggist* **95** (1921), 631. — [2] Com. *Bericht* (German) **1921**, 46. — [3] *Parfum. moderne* **14** (1921), 32. — [4] There seem to be grave discrepancies between the acetylation and ester values and the amount of alcohol, etc. calculated. Besides, $C_{16}H_{18}O$ seems to stand for $C_{10}H_{18}O$. — [5] *Perfum. Record* **11** (1920), 339. — [6] Cf. *Bericht* (German) **1921**, 87. — [7] Comp. *Report* April **1911**, 111.

contain about 60 per cent. of cineole. We do not know, however, what variety of *Thymus* plants contain the oils rich in carvacrol. Holmes may be right in saying that *Thymus Piperella,* L., and *Thymus cœspiticius,* Hoffm., the popular name of which *(pebrella)* indicates a sharp taste like pepper, belong to the carvacrol group. An oil distilled from the fresh herb of *Thymus capitatus,* Lk. (from Granada) contained according to our own investigation 6 per cent. of thymol and a liquid phenol, perhaps carvacrol¹).

This is about all that has been recorded as to the exact botanical origin of the Spanish thyme oils. On the other hand it is known that more than 30 (Willkomm²) states 39) different kinds of *Thymus* are spread over the Iberian peninsula. They partly grow in one and the same district, have great similarity and are perhaps not always differentiated by the gatherers. The thyme plants are gathered above all from the *"tomillares"* (*tomillo* = thyme) which are so characteristic for Spain and, with exception of the Northatlantic zone of the peninsula, occur in the central table-land as well as in the coast provinces and the lowlands along the Ebro, in South Aragon, Catalonia, Valencia, lower Andalusia and Algarbia, covering enormous spaces of uncultivated land. These *"tomillares"* attain their largest dimensions in the table-land, along the Duero, on either side of the central mountain chain and in the East, South and South-West of New Castile. There are thyme, lavender, sage and rosemary heaths, named after the labiate that preponderates. C. Hartwich³) gives a very good description of such a heath: — "On this waste ground of débris the plants grow isolated, though fairly close together, so that the naked soil can be seen everywhere in between. This is the reason why such stretches of land often appear absolutely bare from a distance. The dominating plants, as the name of the steppe indicates already, is a species of thyme (*Thymus Zygis,* L.). The plant forms round little shrubs, perhaps as large as a fist, sometimes, when a stem grows a little higher, miniature trees, like those we owe to the Japanese art of gardening. They have small, needle-shaped leaves, on which the golden-yellow oil glands can be seen through a magnifying glass, and are covered with tiny red flowers. A stem which I examined at home was nine years old."

The *Thymus* species most frequently named and apparently also the most widely distributed in Spain are *Thymus vulgaris,* L., *Thymus Zygis,* L. and *Thymus Mastichina,* L. As E. M. Holmes⁴) determined, *Thymus Zygis* differs from the otherwise similar common thyme, as follows: — The bracts are larger than the ordinary leaves, the whirls of whitish flowerets from an uninterrupted spike and no axillary or terminal heads as with *Thymus vulgaris.* According to Willkomm⁵) the common thyme is to be found in Navarra, in the plain of Pamplona, along the Duero and the Iberian central mountain chain, in the Nord-West of Guadalajara and in the mountainous regions of Catalonia and Valencia, whereas *Thymus Zygis* occurs in the North of Old Castile, near Alar del Rey (Palencia) in the upland ol Murcia in New Castile, in the Vega of Granada, in the Sierra Nevada and in the uncultivated coast regions of the provinces of Cadiz and Huelva. — *Thymus Mastichina* grows on waste ground and by the side of paths and fields in Cantabria, in the slate mountains of Asturia and Leon, in the northern table-land (together with *Thymus vulgaris*), in the lavender heaths of New Castile along the central mountain chain (together with *Thymus Zygis*), on sandy soil between Almeria and the Bay of Gibraltar, on the dry calcareous hills round Granada, and in the *"tomillares"* of the coast zone of Cadiz and Huelva (together with *Thymus Zygis*). Of

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¹) *Bericht* October 1889, 56. — ²) Engler, *Die Vegetation der Erde. Grundzüge der Pflanzenverbreitung auf der iberischen Halbinsel.* By R. Willkomm. 1896. — ³) Spring holidays in Spain. *Apotheker-Ztg.* 21 (1906), 842. — ⁴) *Loc. cit.* — ⁵) *Loc. cit.*

the other species the following are mentioned: — *Thymus hirtus*, Willd., which thrives in Central and southern Spain, on the calcareous hills round Granada and in the lower regions of the Pinsapo Forest, *Thymus hyemalis*, Lange, in south-eastern Spain, *Thymus cephalotus*, L., in Valencia, in lower Asturia and, according to Dorronsoro[1] in Almeria, *Thymus cæspiticus*, Brot., in Estremadura and Galicia, *Thymus Piperella*, L., in Valencia on rocky slopes, *Thymus cerpylloides*, Bory, *(Samarilla)* in the alps of the Sierra Nevada.

To quite another species belongs the so-called Andalusian thyme *(Tomillo andaluz = tomillo carrasqueno)* or *Corydothymus*, which according to Blas Lazaro[1] is *Corydothymus capitatus*, Rchb. B. Dorronsoro[2] writes about it as follows: — "Various kinds of thyme are distilled in Spain, *viz.*, the *tomillo corriente* (common thyme) = *tomillo aceitunero* (olive thyme) = *Thymus vulgaris*, L., the *tomillo risquero* (thyme of the rocks) = *Thymus Zygis*. L., the *tomillo sanjuanero* (St. John's thyme) = *Thymus hyemalis*, Lg., and the *tomillo carrasqueno* (holm-oak thyme) or *tomillo andaluz* (Andalusian thyme), which latter, however, is no real thyme, but *Corydothymus capitatus*, Rchb., belonging to an allied species."

In August 1915, we examined in our research laboratory a Spanish oil from Barcelona, on whose botanical origin, unfortunately, nothing definite could be ascertained. Since only very little positive is known as to the chemical composition of the Spanish oils, the results of the following investigation gave no clue concerning the botanical source of the oil. Owing to the war, the work had unfortunately to be discontinued and was terminated only before long, when the oil had been left standing for nearly six years (protected from direct light) after having been fractionated and freed from phenols by treatment with dilute caustic lye.

The original oil showed the following constants: — d_{15° 0.9297, $\alpha_D + 0^\circ\,35'$, soluble in 3.5 vols. and more of 70 per cent. alcohol; phenols 45 per cent., for the greater part thymol.

The most volatile fraction of the b. p. 130 to 132° smelled of *amyl alcohol* and gave the characteristic naphthylurethane, m. p. 51 to 52° obtained by us on a previous occasion. In the fractions of b. p. range 132 to 150° we suspected owing to their amylaceous smell the presence of *amylcarbinols*. Since they consisted doubtlessly of mixtures, contaminated possibly with small amounts of amylic or similar ketones, we refrained from further isolation and identification. We only by way of experiment, succeeded in isolating a naphthylurethane, m. p. 47 to 48°. We were unable to prove the existence of a ketone, nor the formation of such by oxidation with bichromate solution.

A small fraction, b. p. 145 to 150° (d_{15° 0.8495, $\alpha_D + 3^\circ\,28'$, n_{D20° 1.45052), yielded on benzoylation with the aid of pyridine a benzoate, b. p. 134 to 135° (6 mm.), which on saponification gave rise to an alcohol with the characteristic odour of *β,γ-hexenol.* This alcohol had previously[3] been obtained by us in shape of its phenylacetate from the last runnings of Japanese peppermint oil. Although the oil showed the same boiling point (156°) as the above-mentioned alcohol, we were unable to raise the melting point of the naphthylurethane beyond 58 to 60°, whereas the derivative of the pure alcohol from peppermint oil melts at 72°. In spite of this discrepancy we do not hesitate to accept the identity of the alcohol with β,γ-hexenol. A closer examination carried out with more material will in all probability confirm this identity and thus prove the existence of free β,γ-hexenol in Spanish thyme oil.

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[1] Cf. *Bericht* (German) **1921**, 87. — [2] *Estudio químico de esencias naturales españolas.* Madrid **1919**, p. 134. — [3] *Report* **1918**, 39; Walbaum, *Journ. f. prakt. Chem.* II. **96** (1918), 245.

In the next fractions we found after repeated, careful fractionation a *new terpene* with a carrot-like odour and the following constants:—

1. B. p. 155°: d_{15° 0.8533, $\alpha_D + 4^\circ 50'$, n_{D20° 1.46201
2. B. p. 155°: d_{15° 0.8535, $\alpha_D + 4^\circ 58'$, n_{D20° 1.46221
3. B. p. 155 to 156°: d_{15° 0,8537, $\alpha_D + 4^\circ 35'$, n_{D20° 1.46231.

The values obtained on combustion pointed to a terpene $C_{10}H_{16}$:—

0.1822 g. substance gave 0.5879 g. CO_2, 0.1958 g. H_2O.

	Found	Calc. for $C_{10}H_{16}$
C	87.98 per cent.	88.23 per cent.
H	11.93 per cent.	11.77 per cent.

Mol. refr. found	calc. for $C_{10}H_{16}/\overline{_2}$
43.89	43.51.

The nitrosochloride, purified by means of chloroform and methyl alcohol, shows a strong tendency to decompose and can therefore be prepared and purified only in small amounts. Decomposition starts at about 85° in a very sudden and violent manner. The piperidide melts at 194 to 195°, the nitrolbenzylamine indistinctly from 105 to 108°; the anilide was not obtainable, neither a solid nitrosate. When dissolved glacial acetic acid and cooled down the terpene adds somewhat more than two atoms of bromine; the resulting bromide remains oily. Likewise, the hydrochloride obtained by saturating, in glacial acetic acid solution, the terpene with hydrogen chloride gas was liquid. On trying to hydrate the terpene by action of acetic and sulphuric acids resinification resulted. When oxidized by means of permanganate solution, with cooling by ice (according to the method for obtaining pinonic acid), the terpene gave rise to a neutral oxidation product soluble in water and chloroform, which did not distil without decomposing and was therefore not yet obtainable in the crystalline state. On further oxidation with neutral permanganate at 100° there was obtained, in addition to oxalic acid, m. p. about 100°, and acetic acid (Ag estimated in the silver salt 64.20 per cent.), an acid which decomposed on distillation *in vacuo* and which evidently was not a ketonic acid. Treatment with dimethyl sulphate yielded no ester. Details as to the chemical structure of the terpene are to be expected only after closer investigation. We wish to add that this oil offered no clue for the presence of α-pinene, in contradiction to another oil which years ago¹) we found to contain that terpene. Considering the great variety in the botanical origin of the Spanish thyme oils this different behaviour is by no means surprising.

A very small amount of *camphene* is present in the Spanish oil. It was identified by treating the fractions boiling above 157° in the usual manner with acetic-sulphuric acid, when a trifle of *iso*bornyl acetate (b. p. 82 to 88° at 6 mm.; sap. value 202) was isolated by fractionation. The free *iso*borneol obtained therefrom by saponification melted at 208 to 212°.

β-Pinene was likewise a constituent of the oil. After oxidising a fraction b. p. 165 to 169° with alkaline permanganate a hydrocarbon with the following constants was regenerated:—b. p. 163 to 167°, d_{20° 0.8520, $\alpha_D + 3^\circ 45'$, n_{D20° 1.46609, mol. refr. found 44.02, calc. 43.5. On further oxidation with permanganate is yielded nopinic acid, m. p. 126 to 127°. The hydrocarbon occurs in minute quantity only.

A hydrocarbon fraction, b. p. 165 to 168° (d_{15° 0.8567, $\alpha_D + 3^\circ 57'$, n_{D20° 1.47141) which on saturating with hydrogen chloride gas and after some standing had yielded

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¹) *Report* October 1894, 57.

terpinene dihydrochloride, m. p. 52°, was suspected to contain sabinene. However, on oxidation with alkaline permanganate solution, no sabinenic acid was obtainable.

p-*Cymene* could be proved to be present only after many fruitless attempts, by oxidation of fractions b. p. 175 to 179° with strong permanganate solution, when α-hydroxy*iso*propylbenzoic acid, m. p. 153 to 154°, was the result. On boiling with strong hydrochloric acid the difficultly-soluble propenylbenzoic acid, m. p. 160 to 161°, was formed. The amount of cymene present is exceedingly small. As far back as 1856 Lallemand¹) was able to prove the presence of *p*-cymene in a thyme oil. However, it must remain an open question whether in this case an oil of different botanical origin was under investigation or whether the *p*-cymene had been formed, by a secondary process, from terpinene, an important constituent of the oil.

γ-Terpinene is the main constituent of the phenol-free oil and could be traced in all sub-fractions b. p. 176 to 183°. All of these fractions gave on saturation with hydrogen chloride gas in glacial acetic acid solution, an oily hydrochloride which either was precipitated by addition of water or was obtained on evaporation of the solvent in an open dish after some standing, and could be brought to solidification by strong cooling and additionally after inoculation. When crystallized from methyl alcohol the dihydrochloride melted at 51 to 52°, and in mixture with the corresponding derivative of dipentene very considerable depression of the melting point was observed. From various of the afore-mentioned subfractions there was obtained, on oxidation with alkaline permanganate in the cold, the erythritol $C_{10}H_{20}O_4$ characteristic of γ-terpinene; m. p. 236 to 237°. On boiling with dilute sulphuric acid in a current of steam a smell of phenols (thymol, carvacrol) was noticed. When several fractions (b. p. 175 to 179°; 176 to 178°; 177°) were brominated in absolute ethereal solution, after being chilled down to freezing mixture temperature, separation of a solid, slightly yellow bromide was repeatedly observed which, however, on suction or on spreading on cooled porous plates decomposed rapidly with liquefaction and evolution of hydrogen bromide. Since just these fractions yielded γ-terpinene dihydrochloride in good amount it might have been the case of a bromide of γ-terpinene. Possibly the investigators working on terpinene have hitherto overlooked the fact that γ-terpinene, in absolute ethereal solution at reduced temperature forms a bromide which is unstable at ordinary temperature when exposed to the air. That α-terpinene was absent was concluded from the non-formation of the nitrosite; likewise we were unsuccessful in obtaining, by oxidation with alkaline permanganate, the dihydroxy dimethyladipic acid characteristic of α-terpinene which in many cases, besides γ-terpinene, is a constituent of essential oils.

Of *alcohols*, the following were found to be present: — *linalool, borneol, terpinenol*-4, and *geraniol*.

The first-named alcohol was found in fractions of the b. p. 77 to 78° (6 to 7 mm.) and the sp. gr. d_{15° 0.8975 to 0.8991 which were separated from fractions containing borneol by sharp fractionating. To judge from the odour, an oil of the b. p. 197 to 199.5° and the sp. gr. d_{15° 0.8750 consisted of fairly pure linalool from which the phenylurethane, m. p. 65°, was obtained without difficulty on treatment with phenyl*iso*cyanate. Oxidation with bichromate mixture yielded citral.

l-*Borneol* separated off in the solid state from the fraction b. p. 86 to 102° (8 mm.) when distilling *in vacuo*, and was identified by its odour, its m. p. 204°, and by the formation of camphor on treatment with bichromate mixture.

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¹) *Jahresber. d. Chem.* 9 (1856), 616; acc. to *Annal. de Chim. Phys.* (3) 49 (1857), 148.

Fractions of the b. p. 86.5 to 91.5° and the sp. gr. 0.9403 and 0.9363 showed the characteristic smell of terpinenol reminding slightly of terpineol. Since they contained additionally a small amount of borneol which could not be removed by freezing-out the presence of terpinenol, an alcoholic connected structurally with terpinene and therefore often found in oils containing this terpene, had to be proved by oxidizing it, by means of cold 1 per cent. permanganate solution, to the glycerol $C_{10}H_{20}O_3$. The neutral product obtained hereby (b. p. 160 to 165° [9 mm.]) solidified soon when triturated with chloroform and ether. Whereas, however, Wallach[1]) found the m. p. of the glycerol from terpinenol-4 to be 114 to 116° (glycerol from terpinenol-1, m. p. 120 to 121°), the glycerol obtained by us melted already below 100°, thus proving that the body was not uniform. Only after repeated fractional crystallization it was possible to isolate small amounts of the body with the m. p. 111 to 113°. When heated with dilute hydrochloric acid in a current of steam it yielded, in addition to cymene, carvenone; semicarbazone, m. p. 201 to 202°. The sublimate of the glycerol melted at 128 to 129°. A somewhat larger amount of the glycerol was prepared and transformed, by oxidation with alkaline potassium permanganate, into the α,α'-dihydroxy-α-methyl-α'-*iso*propyl adipic acids of the m. p. 205 to 206° and 188 to 189°. Although we did not succeed in separating the resulting mixture of the active and the inactive acid (m. p. 195 to 200°) into the separate acids with the correct melting point, it was possible to isolate, from the mixture of bilactones obtained by heating the acid mixture to 200° (m. p. 65 to 71°), the bilactone, m. p. 70 to 72°, corresponding to the acid m. p. 188 to 189°, by resorting to fractional crystallization. This bilactone easily passed over, on heating with caustic potash, into the acid m. p. 187 to 188°.

A further proof for the presence of *terpinenol*-4 in the fraction mentioned above was furnished by the formation of terpinene dihydrochloride, m. p. 51 to 52° when the solution in glacial acetic acid was saturated with hydrogen chloride gas. However, we were unsuccessful in attempting to prove the presence in the terpinenol-containing fraction of α-terpineol, which would account for the unsharp melting point of the glycerol $C_{10}H_{20}O_3$ owing to a possible admixture of the glycerol of α-terpineol (m. p. about 121°). It may, therefore, be taken for granted that the incorrect melting point of the neutral oxidation-product may be ascribed to the low content of borneol in the terpinenol fractions.

Small amounts of *geraniol* were found to be present in fractions boiling between 91.5 and 102° (7 mm.); d_{15° 0.9259; faint odour of geraniol. On treatment of the solution in benzene with phthalic anhydride and subsequent saponification of the resulting solution of the ester-salt, an oil, b. p. 225 to 231°, with a pronounced odour of geraniol was formed. It yielded a diphenylurethane, m. p. 82°; on oxidation with bichromate solution, citral was the result.

The high-boiling fractions (b. p. 102 to 106° [7 mm.]; d_{15° 0.9326 to 0.9386) were not entirely free from thymol. After the phenol had been removed and the liquid distilled over sodium, a sub-fraction showed the following properties:—b. p. 259 to 264°; d_{15° 0.9105; $\alpha_D + 7°54'$. On heating with glacial acetic and sulphuric acids, followed by steam-distillation, caryophyllene alcohol, m. p. 94 to 95° was formed, so that the presence of *caryophyllene* in the sesquiterpene fraction was rendered probable. In addition, small amounts of a second sesquiterpene and possibly also of a sesquiterpene alcohol seemed to be present in this Spanish oil.

Hence, the following bodies, besides thymol, have been proved to be important constituents of the oil in question:—a new terpene, b. p. 155°, camphene, γ-terpinene,

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[1]) *Liebig's Annalen* **350** (1906), 169.

l-borneol, linalool, and terpinenol-4; amyl alcohol, amyl carbinols, β,γ-hexenol (?), β-pinene, *p*-cymene, geraniol, and caryophyllene are likewise present. Hitherto, the following constituents of Spanish thyme oil (however, of different botanical origin) had been found:—α-pinene, *p*-cymene, borneol, and linalool.

From the dry herb of *Thymus vulgaris*, L., collected in July near Terracina, province of Rome, P. Leone and E. Angelescu[1]) obtained by steam-distillation 1.06 per cent. of a dark red oil with a strong aromatic odour and the following constants:—$d_{4^\circ}^{13.5^\circ}$ 0.9250, α_{22° — 2.40° (taken in white electric light), n_{D22° 1.49646, a. v. 3.5, sap. v. 14.9; ester v. 11.4, corresponding to 4 per cent. linalyl acetate. Steam-distillation being repeated, the constants of the lemon-yellow oil were:—$d_{4^\circ}^{13.5^\circ}$ 0.9194, $[\alpha]_{D28^\circ}$ — 3.57°, n_{D26° 1.49505.

The phenol (*thymol*. m. p. of the nitroso derivative 141 to 142°) was removed by shaking with 5 per cent. caustic soda solution. Thymol estimated, 38 per cent., according to the iodine method of Kremers and Schreiner. The non-phenolic part of the oil showed, after acetylation, the sap. v. 112, corresponding to 30.8, and 14.1 per cent. when calculated on the entire oil. After repeated fractional distillation under ordinary pressure the following fractions were obtained:—1. up to 165° (1.3 per cent.); 2. 165 to 175° (23.1 per cent.); 3. 175 to 185° (30.8 per cent.); 4. 185 to 195° (6.5 per cent.); 5. 195 to 205° (5.5 per cent.); 6. 205 to 225° (4.8 per cent.); 7. 225 to 235° (10.6 per cent.). After boiling fractions 2 and 3 for five hours with sodium, the authors succeeded in obtaining 13 per cent. (calculated on the entire oil) of a fraction boiling at 171 to 176° which consisted nearly entirely of *cymene* (hydroxy*iso*propylbenzoic acid, m. p. 156 to 157°). The free alcohol seemed to be a mixture of borneol and linalool, which the authors, however, were unable to identify.

From a drug which in its morphological and anatomic characters coincided completely with *Thymus vulgaris*, L. R. Kofler[2]) obtained an oil which differed largely from thyme oil owing to a content of *cineole* and containing but very little, if any, of thymol. The author takes this fact for a further proof for the extraordinary variability of the species of the genus *Thymus* also in their chemical behaviour[3]).

Turpentine Oil.—There are in the main three species of *Pinus* used in the United States for the production of turpentine; *viz.*, *Pinus palustris*, Mill., which supplies the largest quantity by far, *Pinus heterophylla* (Ell.), Sudw., and *Pinus echinata*, Mill. The Bulletin No. 898 (1920) of the U. S. Dep. of Agriculture[4]), which contains much useful information on the turpentine industry of country, names in addition to *Pinus palustris* and *Pinus caribæa (heterophylla)* also *Pinus ponderosa*, Dougl., (Western yellow pine)[5]) as being tapped for turpentine. According to this bulletin, about 75 per cent. of the world's supply of turpentine is produced in the United States, the relative production in the various States being about as follows:—Florida, 37 per cent.; Georgia 19 per cent.; Louisiana, 15 per cent.; Alabama, 12 per cent.; Mississippi, 9 per cent.; Texas, 7 per cent.; North and South Carolina, less than 1 per cent. Formerly North Carolina produced the bulk of the world's supply of turpentine, but now its pine forests are almost exhausted.

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[1]) *Gazz. chim. ital.* **51** (1921), II. 391. — [2]) *Pharm. Monatsh.* **1921**, N° 3. Acc. to *Pharm. Ztg.* **66** (1921), 484. — [3]) Dorronsoro found likewise in Spanish thyme oils originating from *Th. Mastichina*, L. and *Th. cephalotus*, L. up to 60 per cent. of cineole by the resorcinol method. Compare also p. 65 of the present *Report*. — [4]) *Journ. Soc. chem. Ind.* **40** (1921), R. 165. — [5]) Comp. also *Report* April **1913**, 101. According to Engelmann, a botanist who died in St. Louis (Missouri) in 1884, *Pinus ponderosa* is the most widely spread pine of the West in California and Oregon, thriving on low and high mountains, even also in the plain, on sandy-gravelly soil. **Beissner**, *Handbuch der Nadelholzkunde*, 2nd edition, p. 387.

The distilling plant is simple and has not been improved materially during the last 50 to 60 years; it consits of a copper still of 500 to 1000 gallons capacity, with a still-head connected to a large copper condensing-coil cooled in water. From 7 to 14 barrels of oleo-resin go to make a charge, depending on the nature of the oleo-resin and the size of the still. This is heated over an open fire. When most of the water originally present in the oleo-resin has passed over, as shown by the peculiar sound which is heard close to the tail-pipe of the condenser coil, a small stream of water is admitted to the still. The yield of oil varies from 16 to 22 per cent. It is mostly shipped in wooden barrels, treated internally with two coats of glue and holding 50 to 53 gallons. In the more western States the larger producers employ tank-cars of 5 to 16 thousand gallons capacity. On arrival at the primary markets each barrel or tank-car is inspected as to quality and volume.

The total production in the U. S. A. for the 1919 season amounted to 366000 casks (50 galls.) of turpentine oil and 1237000 barrels (500 lbs.) of rosin; during 1920 up to August 1st, 237155 casks of turpentine oil and 712387 barrels of rosin were produced, the estimated production for the rest of the season being 233876 casks of turpentine oil and 739679 barrels of rosin.

At present a little less than 10 per cent. of the total is wood turpentine obtained from stumps and dead or fallen timber by steam or destructive distillation; this source of turpentine is becoming more important.

As per a statistics of the Turpentine and Rosin Producers' Association[1] the U. S. A. supplied before the war about 85 per cent. of the world's requirements of naval stores. At present, the percentage is only 62, the remaining 38 per cent. being contributed by France, Mexico, British India, Spain, Italy and other countries. Especially France has increased her production during the last four years. In 1920/21 it amounted to 250000 barrels (50 gals.) of turpentine oil and 875000 barrels of rosin. Spain supplied twice the quantity of previous years; *viz.*, 41000 casks of turpentine oil. The exports of the U. S. A. in 1921 amounted to 73125 casks of oil and 508334 barrels of rosin (500 lbs.), as compared with an average of 359375 casks of oil and 1354068 barrels of rosin in the last ten years before 1914.

In Central and West Durango (Mexico), there are about 15000000 acres of pine forests, the larger part of which is owned be the Federal Government. As the material is fit for the production of turpentine, an American company erected there a modern distilling plant. The trees can be tapped for three to four years running. Each trunk yields during one season more than one quart of pure, white turpentine oil and 6 lbs. of rosin, the quality of which is not inferior to the products of other countries[2].

Spain's turpentine industry[3] is in the hands of the *Union Resinera Española*, one of the largest and most powerful trusts of the country. This company's report (1919) contains the following figures:—

Production	Rosin	Turpentine oil
1915	15054.593 tons	4331.429 tons
1916	16238.545 „	4868.871 „
1917	14364.773 „	4599.066 „
1918	13918.298 „	4101.384 „
1919	11397.619 „	3647.656 „

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[1] *Drug and Chem. Markets* **10** (1922), 155. — [2] *Drug and Chem. Markets* **9** (1921), 1038. — [3] *Oil, Paint and Drug Reporter* **100** (1921), No. 21, p. 32.

Sales	Rosin	Turpentine oil
1915	15 153.998 tons	4504.281 tons
1916	14 273.563 „	5670.763 „
1917	17 269.470 „	4414.491 „
1918	9 321.734 „	4198.808 „
1919	14 257.651 „	4408.147 „

Spain's exports of turpentine oil, rosin and tar were as follows:—

	1919	1920	in first 4 months 1921
Terpentine oil . .	4 591.216 tons	3 081.873 tons	518.495 tons
Tar	13 041.131 „	12 181.345 „	1039.588 „
Rosin	809.243 „	544.484 „	36.159 „

Portugal produced[1]:—

Year	Rosin	Turpentine oil
1916/17	3000 tons	950 tons
1917/18	4000 „	4200 (?) „
1918/19	6000 „	2000 „
1919/20	6300 „	1800 „
1920/21	12400 „	3600 „

It is reported that there are no stocks of turpentine oil, whereas those of rosin are estimated at about 10 000 tons. Portugal's home consumption is 2000 tons each of turpentine oil and rosin, annually. The pine forests of Portugal (773 000 hectares) cover about the same area as those of south-western France (200 000 hectares in the Gironde, 500 000 hectares in the Landes and 50 000 hectares in the Lot-et-Garonne).

According to Th. M. Ainscough[2] the Indian production of rosin and oil of turpentine becomes more and more important. It started on a small scale about 25 years ago and, owing to the activity and the skill of the foresters, who were well acquainted with the methods employed in the "Landes" of France *(gemmage à vie* and *gemmage à mort)*[3] developed first in the United Provinces of India and later on in the Panjab to its present state. In 1919 an area of 97 525 acres of pine forest (in the main *Pinus longifolia,* Roxb.) yielded 4615 tons of oleo-resin, from which 2400 tons of rosin and more than 156 000 gallons of turpentine oil were prepared[4].

F. Henrich[5] reports on an investigation of pine balsams (*Pinus silvestris,* L.), carried out conjointly with A. Pfotenhauer and under the assistance of F. Pensel. Generally speaking the samples, which came from the neighbourhood of Erlangen and had been collected in different months of 1917 and 1918, had the same composition:—$d_{40^\circ}^{20^\circ}$ 0.8560, 0.8573, $[\alpha]_{D20^\circ}$ + 16.1, + 13.6°; acid v. 0.61, 0.40; ester v. 1.67, 1.58; sap. v. 1.73, 1.62[6]. The resinous residue of one balsam, collected in August from trees growing on fatter soil, contained even less esters than that of the other balsams. About 22 to 25 per cent. of the balsam were volatile with steam[7]. The turpentine oil whose angle of rotation did not exceed $[\alpha]$ + 28.41°, consisted of a small quantity of β-pinene (nopinic acid,

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[1] *Oil, Paint and Drug Reporter* **100** (1921), No. 21, p. 32. — [2] *Ibidem* **101** (1922), No. 1, p. 32. — [3] Comp. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd edition, vol. II, p. 69. — [4] Comp. also *Berichte* (German) **1920,** 132; **1921,** 48. — [5] *Zeitschr. f. angew. Chem.* **34** (1921), 363. — [6] There seems to be a printer's error, for the sum of the acid and ester values must equal the saponification value. — [7] Comp. *Report* **1916,** 54.

m. p. 126°) and apparently a mixture of *d*- and *l*-α-pinene, in which the *d*-α-compound predominated (nitrosochloride 103°).

The authors found too that the unsaponified fraction of the crude oil of turpentine had a somewhat higher specific gravity than the saponified fractions, but that the optical rotation was not considerably influenced by the saponification. It was impossible to establish what the components of the saponified products were.

One sample of turpentine oil ($d_{4^\circ}^{20^\circ}$ 0.8624; $[\alpha]_{D20^\circ} + 17,13^\circ$, $C = 87.0$ per cent.; $H = 11.12$ per cent.) was exposed to the air and examined from month to month. After six months the constants were:—$d_{4^\circ}^{20^\circ}$ 1.0584, $[\alpha]_{D20^\circ} + 1.44^\circ$, $C = 71.03$ per cent., $H = 9.45$ per cent. In another sample of purified turpentine oil from pine balsam, which had been kept for three years in an Erlenmeyer flask, the presence of small quantities of a peroxide, of acid-like components (not abietinic acid) and of 20 per cent. of resene was proved. (Tschirch found in a six months old, autoxidized French turpentine oil above all a resene-like body in addition to a small amount of resinolic acid. *Arch. d. Pharm.* **238** (1900), 645.) Besides, the authors obtained from this sample a small quantity of a dextrorotatory oil, smelling like menthol, but which it was impossible to examine any further.

M. Vèzes[1]) thinks it possible to determine the proportion of α-pinene and β-pinene (nopinene) in French turpentine oil with the aid of Darmois'[2]) polarimetric method. The proceeding, which it would lead us to far to describe in detail, consists in that the rotatory power of 5 fractions of equal size is determined for three colours. With the aid of the known rotatory power of α- and β-pinene the proportion of the quantities of these terpenes can easily be calculated. Vèzes found in this way that a French oil of turpentine (b. p. 154 to 162° under ordinary pressure, without the less volatile hydrocarbons) contained 80.9 per cent. of α-pinene. It may be added that the author himself thinks the method has not been sufficiently verified yet and that he calls the values found only approximately correct.

F. C. Palazzo, Mina Palazzo and E. Azzarello have published conjointly a series of articles[3]) on investigations of Italian turpentine oil, the results of which have been discussed in part in our previous *Reports*[4]) (on oil of turpentine of *Pinus Pinea*, L., and of *Pinus Pinaster*, Sol.).

One of these articles (no. III by F. C. Palazzo and E. Azzarello) deals with the applicability of Italian oil of turpentine. As has been shown before, the oil obtained in Tuscany[5]) (b. p. 170 to 172°, d_{15° 0.852, n_{D20° 1.474, inflammation point 50°) consists chiefly of *l*-limonene and differs considerably from the products of other countries, which contain α-pinene above all. It is pointed out in the article, why just these properties (lesser volatility, better capacity for dissolving resins, balsams, fats and waxes, elevated inflammation point, &c.) make the Italian turpentine oils very fit and valuable for certain technical purposes, such as the manufacture of varnishes, oil paints, &c. It is further mentioned that the vapours of these oils, contrary to the products containing pinene, do not injure the human organism.

Pinus halepensis, Mill., the turpentine of which might likewise be put to use, also occurs in Italy. M. Palazzo[3]) investigated oils of turpentine, obtained from *Pinus halepensis* in Cecina and Vada. The yield in turpentine which was obtained according

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[1]) *Compt. rend.* **172** (1921), 977. — [2]) *Thèse*, Paris **1911**, p. 53. — [3]) *Le trementine italiane.* Nota I, II, III, IV. From *Annali del R. Istituto Superiore Forestale Nazionale*, vol. II, **1917** and vol. IV, **1919**. As per a reprint kindly sent us. — [4]) Comp. *Report* **1917**, 72; **1918**, 50. — [5]) The turpentine of the different *Pinus* species, among which *Pinus Pinea* preponderates, are not distilled separately.

to the method used in the Landes[1]) in the course of about five months, was approximately 1.3 kilos per tree. If the normal time of seven to eight months was allowed, Palazzo thinks that the output could be increased to 1.8 kilos per tree.

The product yielded on an average about 20 per cent. of turpentine oil with the following properties: — d_{15° 0.8635, $[\alpha]_{D15^\circ} + 46.71^\circ$, n_{D15° 1.4688, soluble in 7 parts of 90 per cent. alcohol, inflammation point 32 to 33°. When subjected to fractionated distillation, the six first fractions (90.4 per cent.) passed over between 154 and 158° and consisted almost exclusively of *d*-pinene. The 7th and 8th fractions boiled from 158 to 160° and from 160 to 163°, respectively.

The methods for detecting and estimating toluene, xylene, solvent naphtha and other coal-tar derivatives in turpentine oil, as suggested by Marcusson[2]) and Krieger[3]) have not been found reliable by V. E. Grotlisch and W. C. Smith[4]) especially if small quantities are concerned. Grotlisch and Smith have therefore contrived a new method, according to which the turpentine oil is first treated with dry hydrogen chloride. The pinene hydrochloride formed is separated from the other liquid, which is then distilled under reduced pressure The unchanged coal-tar oils pass over with the first part of the distillate. This is sulfonated with fuming sulphuric acid and distilled with steam. In the case of pure oil of turpentine, a very small quantity of a dark yellow volatile oil of disagreeable smell is obtained: — index of refraction n_{D20° slightly above 1.500. If any mineral oil is present, an almost colourless product is obtained, having the characteristic mineral oil odour and an index of refraction below 1.500, generally below 1.4800. If coal-tar derivatives were present, they can be recovered as such to the extent of 45 per cent. The quantity present thereof is found therefore by multiplying the result of the analysis with 2.2. — The sulphuric acid used must always have the same concentration and contain 3 to 4 per cent. of free SO_3. Otherwise the results do not agree. This method is not strictly applicable to wood turpentine oil, unless the adulteration exceeds 4 per cent., as small quantities of benzene hydrocarbons occur as normal components of this oil.

With reference to Salvaterra's article "On New Methods of Investigating Turpentine Oil", in which the author declares that Herzfeld and Marcusson's method is not altogether free from objection[5]), J. Marcusson[6]) points out once more the usefulness of his nitric acid test for the determination of light petroleum in turpentine oil. According to these explanations Marcusson's investigations of mixtures of light petroleum and turpentine oil would prove that his method suffices completely for technical purposes. The nitric acid method is applicable not only for turpentine oils, but also for pine oil and pinolene and does not depend upon what sort of light petroleum is present. Even small quantities, such as 2 to 3 per cent. of light petroleum, were still to be detected with his method.

H. Heller[7]) publishes an extract of H. Salvaterra's article on the investigation of turpentine oils[8]) discussed by us already, under the title of "New Methods for the Investigation of Turpentine Oils".

As C. M. Sherwood[9]) reports, the extraction of rosin, pine oil and turpentine from dead pine wood was begun in 1909 by the Yaryan Naval Stores Co. at Gulfport and Brunswick, Ga., Since 1921 this company works conjointly with the Hercules

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[1]) *Gemmage à vie* or *gemmage à mort;* comp. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd edition, vol. II, p. 69. — [2]) *Chem. Ztg.* **36** (1912), 431. — [3]) *Ibid.* **40** (1916), 972. — [4]) *Journ. Ind. and Eng. Chem.* **13** (1921), 792. — [5]) Cf. *Bericht* (German) **1921**, 49. — [6]) *Chem. Ztg.* **45** (1921), 418. — [7]) *Deutsche Parf.-Ztg.* **7** (1921), 131. — [8]) Cf. *Bericht* (German) **1921**, 48. — [9]) *Chem. and Met. Engin.* **25** (1921), 994.

Powder Co.[1]) The combined maximum worked per day is about 1000 tons of wood. As Sherwood declares, it cannot be said that this industry has been profitable up to the present time, but it may nevertheless be called upon to act an important part in future in the production of naval stores. The wood chiefly used is the Southern long-leaf pine *(Pinus palustris)*. The material may be divided in stump wood and top wood, the former being richer in extractable products. It seems to be generally true that the twisted grain wood is richer than the straight grain. The distribution in the roots is also interesting. The lateral roots are very rich in rosin, turpentine and pine oil; the tap root is soft and spongy and contains practically no valuable products. Good land yields 8 to 15 tons of wood per acre, depending on the section of the country. The milled wood is steamed for 3 to 4 hours in an extractor, when all the easily boiling constituents (called turpentine by the author) and about half of the less volatile ones (pine oil) are distilled off. This distillate, consisting of approximately 70 per cent. of light and 30 per cent. of heavy wood turpentine oil is then fractionated. The steamed wood is boiled with a solvent, generally gasoline, in order to obtain the rosin and the heavy oil still left behind. The solvent and the heavy oil extracted are separated from the rosin by repeated distillation.

The light wood turpentine oil obtained that way distinguishes itself by its uniformity and has the following constants: — initial b. p. 154°, constituents boiling below 170° = 90.5 per cent., residue 1 per cent., $d_{15.5^\circ}^{15.5^\circ}$ 0.865, $n_{D15.5^\circ}$ 1.469, flash point (Abel, closed cup) 34°. This wood turpentine oil has not the fragrant, sweet odour of freshly distilled gum turpentine oil.

A high-grade commercial pine oil manufactured at Brunswick, Ga., had the following properties: — boiling range 180 to 225°, $d_{15.5^\circ}$ 0.935, $n_{D15.5^\circ}$ 1.479, residue 3 per cent., colour light straw. According to Sherwood, the composition of pine oil, which resembles turpentine oil very closely, is rather uncertain. We would mention therefore that, years ago[2]) we thoroughly investigated a yellow pine oil, *i. e.*, a wood turpentine oil obtained from the stumps, most likely from *Pinus palustris*, and found the following constituents: *l*-α-terpineol, α- and β-pinene, camphene, *l*-limonene, dipentene, γ-terpinene, cineole, *i*-fenchylalcohol, campher, *l*-borneol and methylchavicol.

Pine oil when first produced was considered practically worthless. In later years, however, it has become valuable in many ways, *e.g.* in the flotation process, as basis of a variety of medicinal and desinfectant solutions and as a solvent in the rubber, paint and varnish industries.

The rosin obtained through the extraction is generally ruby red and consists, like ordinary rosin, chiefly of abietic acid, $C_{20}H_{30}O_2$[3]). The percentage found by analysis were C 78.12, H 9.90 and O 11.98 per cent. Wood rosin is said to have an advantage over gum rosin because of its uniformity and cleanliness.

Also in Germany stumps are used again on a larger scale for the production of turpentine oil. As F. O. Koch[4]) reports, the following yields were obtained from resinous stumps (root wood of *Pinus silvestris*, L.) according to Franz Schmidt's method: 5 per cent. oil of turpentine, 1 per cent. acetone, 8 per cent. tar and 22 per cent. charcoal. Koch then makes some remarks concerning the problem of the production of turpentine and pine oils from stump wood, remarks which are not altogether reliable and invite

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[1]) In 1910 there were 30 plants in the U. S. A., where yellow pine was distilled, in addition to smaller quantities of Norway pine and Douglas fir. Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, p. 98. — [2]) *Report* April **1910**, 103. — [3]) The acid $C_{20}H_{30}O_2$ is pimaric acid. — [4]) *Chem. Ztg.* **45** (1921), 699.

criticism. Link[1] has already found the proper answer, so that we may refrain from going into details. We would only add that the good quality of the French product is due to the peculiar composition of the French turpentine, and to the methods of producing the gum and distilling the oil. Koch's assertion "that an excess of volatile constituents in the gum, the loss of which during the exudation has no great effect" was responsible for the superiority of the French turpentine oil, is absolutely unfounded. As to the author's opinion that the direct production of turpentine oil from stumps had so far been unknown in Germany and other countries, Link remarks that about 40 years ago already an excellent pure turpentine oil has been obtained by steaming resinous wood. Link mentions that he himself constructed a factory in Western Prussia, in 1893, and another in Volhynia, in 1901, where the oil was drawn from the wood in a specially constructed apparatus, before being carbonized. The high costs of production, combined with the competition from abroad, which sent the prices down, prevented the construction of more such plants. He thinks that now conditions have altered somewhat, as more trees are cut in the forests and the competition of other countries is less keenly felt.

The factory in Volhynia, erected by Link, produced in the first four years 1554 tons of turpentine oil, 144.48 tons of pine oil, 10298.4 tons of tar, 1680 tons of acetate of lime (80 to 82 per cent.), 210 tons of wood-spirit (calculated as 100 per cent.) and 12196.8 tons of charcoal, from 168000 cubic metres of wood.

The products offered as turpentine oil in Esthonia during the last three years were, according to J. Schindelmeiser[2], exclusively pine or sulphate oils. The pine oil produced in Esthonia contained from 50 to 75 per cent. of pinene; that from the East was also rich in pinene, whereas the Finnish product contained more cymene. If, like in Finland, the oil is obtained at a higher temperature, cymene forms at the expense of the pinene. The Esthonian crude oil differed greatly in that sometimes up to 75 per cent. could be distilled off with steam, but in some cases barely 20 per cent. The sulphate oil, coming from the Swedish wood pulp factories, but bought and sold as French oil, consisted almost entirely of cymene.

The odour of sulphate turpentine oil can be improved according to L. Schmidt[3] by heating the oil for two hours with sodium peroxide under a reflux condenser. The product is then filtered in order to separate it from the yellow deposit formed and distilled with steam. The turpentine oil thus obtained is said to resemble the French oil.

F. Baum, of Jena University's Women's Hospital, used against certain inflammations injections of the following kind: turpentine oil 4 grams, eucupin 0.2 grams, olive oil 16 grams. As albuminuria was sometimes noticed after this treatment, one must be careful in case of inflammation of the kidneys[4].

As a treatment of spotted fever, A. Brenner[5] recommends oil of turpentine (to be taken every hour in doses of 0.05 to 0.1 gram) or terpin hydrate. Besides, the remedy is to be inhaled.

Valerian Oil. — In Belgium, the costs of the production of valerian root, including farmt-rent, wages, &c., are four times as high as before the war. The 1920 crop is said to be of very good quality, the roots being clean, heavy, of light colour and

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[1] *Chem. Ztg.* **45** (1921), 820. — [2] *Pharmacia* **1921**, No. 3, p. 16. — [3] D. R. P. 340126, dated 27. II. 1919. As per *Chem. Zentralbl.* **1921**, IV. 1016. — [4] *Med. Klinik* **1921**, No. 13. As per *Vierteljahresschr. f. prakt. Pharm.* **18** (1921), 130. — [5] *Münch. med. Wochenschr.* **1921**, p. 992. As per *Therap. Halbmonatsh.* **35** (1921), 642.

likely to keep in good condition for several years. As the cultivation of valerian is no longer profitable enough, the Belgian farmers mean to continue it only, if better prices can be obtained[1]).

Indian Valerian Oil. — Valerian root from the western spurs of the Himalayas contains an essential oil, of which a sample was sent us recently. It behaved as follows: — d_{15° 0.9361, α_D —34° 6′, n_{D20° 1.48712, acid v. 37.3, ester v. 39.8, ester v. after acetylation 69.1, soluble in 0.3 vols. and more of 90 per cent. alcohol, whereas of 80 per cent. alcohol even 10 vols. did not suffice for dissolving the oil. The colour was yellowish green, the odour strong and lasting.

We were told that it came from *Valeriana Wallichii,* DC.

Vetiver Oil. — We stated quite a new kind of adulteration in a Réunion distillate, received some time ago. Among other substances, it contained glycerin acetate, an admixture which we had not expected at first. The oil was conspicuous by its properties: — d_{15° 0.9911, α_D +6° 20′, n_{D20° 1.51862, acid v. 0.5, ester v. 43.5, not yet soluble in 10 vols. of 80 per cent. alcohol. Comparing these figures with those for normal Réunion vetiver oils (d_{15° 0.990 to 1.020; α_D +22 to +37°; n_{D20° 1.515 to 1.527; acid v. 4.5 to 17; ester v. 5 to 20; soluble in 1 to 2 vols. of 80 per cent. alcohol), one sees at once that oil deviates the polarized light far too little, has too low an acid value and too high an ester number, whereas the solubility is absolutely insufficient. As these properties do not tally either with those of vetiver oils from other sources (Fiji Islands, Seychelles), there was sufficient cause for suspecting adulteration. Although we could not say anything definite straight off, we had to refuse the oil. The supplier, most likely in France (we bought the article from a middleman) was very indignant in consequence, but soon assumed a different tone, when we let him know that we had meanwhile succeeded in proving the presence of glycerin acetate in the oil. The following observation had shown us the way. The part of the oil which was insoluble in 80 per cent. alcohol and the soluble part, after having been separated off on adding water to the solution, were both lighter than the original oil. It was therefore evident that the alcohol had also taken up a heavier component which, as water did not separate it off, had to be soluble in water. It was therefore natural to think of glycerin acetate, the presence of which could be proved on closer investigation. It was recognized by its specific gravity (d_{15° 1.1654) and the high saponification value (671.6). The quantity was 5 per cent.

No doubt there was still another adulterant present, for the exceedingly low rotatory power and the insufficient solubility are not fully explained by the above remarks. Cedarwood oil probably had something to do with it, but we had no cause for further investigation, as the oil was taken back.

Oil of the roots of Viola odorata. — One of the oils formed by the decomposition of a glucoside is, according to A. Goris and Ch. Vischniac[2]), the oil contained in the roots of the sweet violet, which was discovered quite by chance. At a place where violets (*Viola odorata,* L.) grew abundantly, the authors noticed quite a strong violet smell, although the plants had no flowers as yet. On closer investigation, it resulted that the somewhat herbaceous and impure violet odour emanated from the fresh roots, when rubbed. Fowl had scratched there, had thus laid the roots bare and damaged them, which caused them to smell. In order to study the matter further, the authors

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[1]) *Chemist and Druggist* **94** (1921), 404. — [2]) *Bull. Roure-Bertrand Fils,* April **1921**, 3.

sterilized 122 kilos of roots, collected near Grasse in March, and extracted them thoroughly with hot alcohol, to which some calcium carbonate had been added. The product was extracted with hot, aqueous acetic ester and the resulting green extract treated with hot water. The watery solution contained the glucoside and part of the already free oil, which was separated with the aid of ether. When some powdered violet root, which had previously been washed with alcohol and ether, was added to the aqueous liquid, a slight alteration of the rotation and the presence of a small amount of essential oil was to be noticed[1].

Only a very few data are given about the oil itself. The yellow, aromatic product was partly soluble in light petroleum. This component proved to be a cristalline mass, which, after having been dissolved in an aqueous solution of sodium carbonate, could be precipitated with hydrochloric acid. On treatment with ether, a cristalline mass was then obtained which gave a green colour reaction with ferric chloride solution.

From the part that did not dissolve in light petroleum, a small quantity of salicylic acid was obtained after saponification with alcoholic potash lye. The authors take it that methyl salicylate was probably present in the roots, as Desmoulière[2] arrived at the same result, years ago, with *Viola tricolor.*

Oil of Vitex trifolia. — On distilling the leaves and twigs of *Vitex trifolia,* L. (*Vitex ovata,* Mak. [?] [Thunb.]), a verbenacea grown in the Ogasawara Islands and Kanagawa Prefecture (Jap. *hamago*), Y. Shinosaki[3] obtained 0.11 to 0.28 per cent. of an oil having a brown colour and a characteristic odour[4]. Three samples of the oil had the following characters: — d_{15° 0.8908 to 0.9141; α_{D20° −39° 6′ to −47° 20′; n_{D20° 1.4707 to 1.5010; acid v. 0 to 1.75; sap. v. 23.38 to 38.70; sap. v. after acet. 40.14 to 53.34. The chief constituents of the oil were *l*,α-pinene, which gave no solid nitrosochloride, camphene (together with pinene: — 55 per cent.), terpinyl acetate (10 per cent., b. p. 84 to 86° at 15 mm.; d_{15° 0.9629; n_{D20° 1.4670); a diterpene alcohol $C_{20}H_{32}O$ or $C_{20}H_{34}O$ (20 per cent., b. p. 165 to 167° at 4 mm.; d_{15° 0.9760; α_{D20° −46° 39′; n_{D20° 1.5143; sap. v. after acet. 42.02). The oil was separated into its three chief constituents by fractional distillation; the middle part might be suitable for perfumery purposes, as it is mainly composed of terpinyl acetate.

Oil of Water-hemlock. — A trial distillation of faded roots of water-hemlock (*Cicuta virosa,* L.) gave us an opportunity of determining some properties of this oil, which is but little known. It was yellow and had a faint odour, which it is difficult to describe. A similarity with water-fennel and celery, noticed by others on a previous occasion[5], could not be stated this time. The following constants were determined: — d_{15° 0.8909, α_D +16° 32′, n_{D20° 1.48480, acid v. 3.7, ester v. 17.7, soluble in about 4 volumes of 90 per cent. alcohol, but with turbidity which, on standing, led to the separation of flakes (paraffin?). The yield amounted to 0.04 per cent.

Wormwood Oil. — F. Rabak[6] publishes the following observations wade with wormwood, *Artemisia absinthium,* L., under cultivation at the Arlington Experimental Farm, Arlington, Virginia, for a period of years. During that time the plant was

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[1] These facts indicate the presence of a glucoside, it is true, but the authors themselves have to admit that it has not been proved as yet. — [2] Cf. *Report* April **1904**, 88. — [3] *Journ. chem. Ind., Japan* **24** (1921), 191. *Journ. Soc. chem. Ind.* **40** (1921), A. 411. — [4] Years ago, a sample of the essential oil of *Vitex trifolia,* L. has been distilled from a specimen growing in the Botanical Garden of Sumatra, which contained cineole. Comp. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. III, p. 409. — [5] Cf. Gildemeister and Hoffmann *The Volatile Oils,* 2nd edition, vol. III, p. 326. — [6] *Journ. industr. and engin. Chem.* **13** (1921), 536.

distilled both in the fresh flowering and in the dry condition, and also at different stages of growth. A number of the oils obtained were subsequently examined in the laboratory and compared from the standpoint of their physical and chemical properties. The conditions of distillation in every instance were identical. The yields of oil from the fresh flowering herb varied with the climatic conditions from year to year, oscillating in the period from 1907 to 1919 between 0.12 and 0.24 per cent. The greater the number of clear and partly cloudy days, the greater was the tendency of the plant to high yields of oil, whereas high rainfall and low temperature apparently tended toward low content of oil. The oils distilled from the dry plants were uniformly darker in colour and stronger in odour. They had a higher ester content (thujyl acetate 35 and 27.3 per cent.) than the ordinary oil (thujyl acetate 32.2 and 24.1 per cent.). It seems therefore that drying favours the formation of ester[1]. The maximum yield of oil was attained during the budding and flowering period. There was a decided decrease in the fruiting stage of the plant (in 1910: — from 0.20 to 0.08 per cent.). The content of free acids (as acetic) and of thujyl alcohol decreased as the plant passed from the budding to the fruiting stage.

Wintergreen Oil. — We would briefly mention two wintergreen oils received from Java (doubtless from *Gaultheria punctata,* Blume), as such distillates are found in commerce from time to time. They were colourless and behaved, as regards odour and constants, very much like the Indian oil of the same botanical origin, described by us some time ago[2]: — d_{15° 1.1873 and 1.1861, $\alpha_D \pm 0^\circ$, n_{D20° 1.53639, acid v. 5.4 and 4.8, ester v. 364.9 (= 99 per cent. of methyl salicylate) and 356.6 (= 96.8 per cent. of methyl salicylate), soluble in 7 and 8 volumes, respectively, or more of 70 per cent. alcohol.

These oils differ from the American distillate of *Gaultheria procumbens,* L., in that they are optically inactive; besides, their aroma is not so fine.

Indian Wintergreen oil. — According to Puran Singh[3], the fresh leaves of *Gaultheria fragrantissima,* Wall., collected in Assam during the winter, gave as much as 0.65 per cent. of oil, or 1.2 per cent. calculated on dry material. The Nilgiri plant gave only 0.12 per cent. of oil from fresh leaves. The plant grows gregariously in the Nilgiris, in Assam and Ceylon, but for a regular supply of the leaves it would be necessary to cultivate it on an extensive scale.

Wormseed Oil. — The demand seems to increase in the Dutch Indies too. As the Dutch Chamber of Commerce in New York[4] communicates, considerably larger quantities of wormseed oil were produced in 1920, mostly in plantations connected with the cultivations of the Government. Nevertheless the home production was not large enough to satisfy the demand.

As so much attention has recently been paid to the East Indian wormseed oil[5], a sample originating from Java was very welcome, as it gave us an opportunity of getting acquainted with that product. The following constants were observed, d_{15° 0.9662, $\alpha_D + 0^\circ 4'$, n_{D20° 1.47867, acid v. 0.9, ester v. 9.8, soluble in 5.8 vols, and more of 70 per cent. alcohol, there being a slight turbidity in the beginning. The odour differed somewhat from that of the American oil, the smell of ascaridole being less strong.

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[1] It must be taken into consideration, however, that the volatile constituents escape during the drying process. — [2] *Report* October **1911**, 97. — [3] *Perfum. Record* **12** (1921), 51. — [4] *Holland and her Colonies* **1** (1921), No. 7, page 15. — [5] Comp. *Berichte* (German) **1920**, 59; **1921**, 15.

Our friends say that in Java only the seeds are distilled. The oil obtained in a comparatively small quantity is not exported but consumed in the country. It is considered inferior to the American product, as it is said to contain less ascaridole. The wormwood cultivation in Java is rather difficult, as the seeds do not ripen at the same time. The plant itself remains low and herbaceous. Plantations on a large scale have been abandoned, as it was recognized that it would be impossible to compete with the United States under normal conditions.

Chenopodium herb *Oil.*—As is known, the American wormseed oil is distilled from the seeding plant of *Chenopodium ambrosioides,* L., var. *anthelminticum,* Gray. We had an opportunity of late to distil the herb by itself and shall here report on our experience.

Fresh chenopodium herb, without seeds, yielded 0.0057 per cent. of an olive-green oil showing the following constants, d_{15° 0.8552, $\alpha_D + 1^\circ$, n_{D20° 1.48141, acid v. 2.7, ester v. 28.9, soluble in 5 vols. and more of 90 per cent. alcohol with slight opalescence.

From a second sample of herb, just beginning to seed, 0,034 per cent. of a brown oil were obtained, which had a higher specific gravity and a higher index of refraction and dissolved a little better than the one before mentioned: d_{15° 0.8795, $\alpha_D + 1^\circ 15'$, n_{D20° 1.48403, soluble in 1.4 vols. and more of 90 per cent. alcohol.

The extremely feeble odour was remarkable with both oils. They lacked almost completely the typical smell of ascaridole, so that it is to be supposed that they contained very little of this essential constituent. This would account perhaps for the low specific gravity and the insufficient solubility. It is remarkable too that the oils were dextrorotatory.

We are unable so far to explain these abnormalities. It is questionable whether they are only due to the absence of seeds, or whether the fact that the herb was grown in Germany, under conditions of climate and soil differing from those in America, is responsible for them.

Since some confusion exists as to the question to which constituent of the oil the anthelmintic action is due, Th. A. Henry and H. Paget1) undertook a re-examination of the oil. Six samples of commercial oils were used, with the constants:—$d_{15^\circ}^{15^\circ}$ 0.9582 to 0.9723, $[\alpha]_{D15^\circ} - 4.5$ to -6.8°. The oils were separated by distillation under 15 mm. pressure into three fractions:—1) b. p. below 84° (25 per cent.), 2) 84 to 104° (15 per cent.), 3) 104 to 118° (55 per cent.), the residue (5 per cent.) being chiefly ascaridole glycol. The first fraction consisted mainly of hydrocarbons, furthermore butyric acid (Ag-salt), methyl salicylate (below 5 per cent.; m. p. of the salicylic acid 156°; benzoate of the ester, m. p. 83°). The hydrocarbons were α-terpinene (nitrosite, m. p. 155°), a new lævorotatory terpene (with the approximate constants: b. p. 177 to 178° [760 mm.], d_{15° 0.847, $[\alpha]_{D15^\circ} - 57^\circ$, n_{D20° 1.484; tetrabromide, m. p. 117°, inactive) and *p*-cymene. The second fraction contained hydrocarbons and ascaridole, the third consisted of nearly pure ascaridole (b. p. 108 to 110° [15 mm.], d_{15° 1.0120, $[\alpha]_{D15^\circ} - 0.5^\circ$).

According to the statements of the authors, sylvestrene, limonene, phellandrene, safrole and camphor were absent. The new terpene, which could not be separated from α-terpinene and *p*-cymene, yielded on oxidation with potassium permanganate acetic acid, *iso*butyric acid and a minute amount of a volatile acid, m. p. 117°, crystallising in long, slender needles, but insufficient for examination. On oxidising α-terpinene with potassium permanganate in acetone solution, the authors obtained two optically inactive forms of α,α^1-dihydroxy-α-methyl-α^1-*iso*propyladipic acid (m. p. 203

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1) *Journ. chem. Soc.* **119** (1921), 1714. From a copy kindly furnished by the authors.

to 204° and 189°), which Wallach1) had obtained formerly when oxidising terpinen-4-ol from marjoram oil. Wallach's acid of the m. p. 205 to 206° was, however, optically active.

From two samples of Indian chenopodium, *Ch. ambrosioides* and *Ch. anthelminticum,* the authors distilled 0.17 and 0.24 per cent. oil having the constants $d_{15^\circ}^{15^\circ}$ 0.9399, $[\alpha]_{D15^\circ} + 0.07^\circ$ and $d_{15^\circ}^{15^\circ}$ 0.9080, $[\alpha]_{D15^\circ} - 9.6^\circ$ respectively.

We extract the following from P. van der Wielen's2) treatise on chenopodium oils: — According to the publications of Schüffner and Vervoort3) American wormseed oil quickly gained a world-wide fame as a remedy against the widely-spread hook-worm disease, owing to the support of the Rockefeller Institute. Said complaint is caused by two intestinal worms, namely *Ankylostoma duodenale,* found in the mines not only north of the Alps, in France, Germany, Austria, Hungary, Belgium and England, but also in subtropical and tropical climates, and the perhaps still more dangerous *Necator americanus,* occurring in the South of North America, in Puerto Rico, Cuba and Brazil. The disease may be brought about by drinking impure water, containing larvæ of the worms, or by infection through the skin. In places where the skin is thin, as for instance on the ankles, the larvæ penetrate into the body, pass through the blood-vessels, the lungs, the larynx and the esophagus into the digestive system and there develop. The miners generally get the disease in this way.

However successful a remedy chenopodium oil may be, its noxious qualities ought not tn be underrated, for it may quite unexpectedly give rise to cases of poisoning. In the report of the Rockefeller Institute of February 1921, Darling and Smillie mention three such cases, caused by a chenopodium oil that had produced no ill effect with other patients. The maximum dose for grown-up people ought to be fixed at 3 cc. of the oil. On the other hand, the efficacity is said to have sometimes been less than expected, of proof that the anthelmintic properties of the commercial oils, the constants of which were not always the same, could be very different4).

L. Sullivan5) has made a detailed investigation into the manufacture of oil of wormseed in Carroll County, Maryland. The belt in which the wormseed *(Chenopodium ambrosioides)* is grown, he says, extends from a short distance north of Weston almost due south to Woodbine, being about 15 miles long and approximately 4 miles wide. The plant grown outside this belt is said to be far less productive of oil, and the product is not so good. There are several hundred farms on which the herb is cultivated systematically and gathered, the crop being taken to distilleries, of which there are about a dozen in the county. The largest individual farm does not exceed 13 acres, and the biggest company-owned plantation is about 20 acres. The annual production varies from 10000 to 40000 lbs., whereas it was only 2800 lbs. in 1910 and 5000 lbs. in 1911. The 1920 yield is stated to have been relatively small, but the acreage cultivated was larger than usual. The better the soil is worked and manured, the higher the percentage of oil in the plant. The yield in oil may run from 30 to 100 lbs. per acre.

According to Chevalier6) *Chenopodium ambrosioides,* L., *Ch. anthelminticum,* L. and *Ch. suffruticosum,* Willd., yield anthelmintic volatile oils, whereas *Ch. spathulatum,* Sieb. and *Ch. retusum,* Moq., are less important. — Van der Wielen7) stated that plants grown

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1) *Liebig's Annalen* **356** (1907), 212. — 2) *Pharm. Weekblad* **58** (1921), 1080. As per a reprint kindly sent us. — 3) Cf. *Report* **1919**, 113. — 4) This is quite possible, as the distillation of American wormseed oil is rather difficult and may lead to inferior products. Adulterations with ineffective substances are also frequent and sometimes even absolutely valueless artificial mixtures are offered. Cf. *Berichte* **1921**, 53, **1920**, 63; *Report* **1919**, 61, &c. — 5) *Perfum. Record* **12** (1921), 39. — 6) *Bull. des sciences pharmacologiques,* March **1921**. — 7) *Loc. cit.*

in India from seeds of the *Chenopodium ambrosioides* type yielded oils of varying efficacy. Whereas American oils are only lævorotatory ($\alpha - 2^\circ 49'$ to $- 8^\circ 50'$, we have observed $- 4^\circ$ to $- 8^\circ 50'$) the Indian oils had a rotatory power of from $- 2.34^\circ$ to $+ 0.50^\circ$[1]). 100 kilos of fresh herb, grown by the author in Amsterdam, yielded on distillation 5 grams of oil. After having been rectified *in vacuo* at 48° (55 mm.)? its index of rotation was $\alpha + 0.74^\circ$. By extraction with ether, van der Wielen obtained from Indian (Atjeh) chenopodium seeds an oil, the rotation of which was $\alpha + 1.05^\circ$. These experiments confirm Wirth's assertion that the rotation to the left increases if the oil is heated for some time[2]). Van der Wielen therefore thinks it probable that an oil of *Chenopodium ambrosioides,* var. *suffruticosum,* Willd., obtained without heating to a higher temperature, would be dextrorotatory or inactive, but not lævogyrate[3]).

The author further calls attention to the fact that other physical properties of the oil likewise alter on heating. The specific gravity decreases, the index of refraction rises and the solubility in alcohol and acetic acid is lessened. The above-mentioned extracted oil of Atjeh seeds, for instance, had the following constants: d_{18° 1.008, n_{D18° 1.4735, soluble in 5.5 vols. of 60 per cent. acetic acid. As these constants resemble those of ascaridole rather much, and as *p*-cymene occurs in chenopodium oil, the author's opinion is that on heating the oil ascaridole is transformed into *p*-cymene, hydrogen being split off. The explosion-like decomposition of ascaridole when heated, noticed by Kremers, is supposed to support this theory.

Through experiments with animals, M. C. Hall and H. C. Hamilton[4]) have proved that the lower-boiling fractions of American wormseed oil have the same vermifugal efficacy as the higher-boiling constituents, without possessing the dangerous by-effects as cause inflammation and bleeding of the intestines. Tijssen[5]) was able to confirm these observations through clinical experiments. He prepared by distillation of an (Indian?) chenopodium oil (d 0.968) a fraction of the specific gravity of 0.951 and a residue of d 1.04. Both preparations were administered to patients suffering from hook-worm disease. In the first experiment the lower-boiling fraction resulted to be very efficacious, the higher-boiling one not. Later experiments had not quite the same result. Distillates free from ascaridole, administered three times in doses of 16 drops each, ejected 77 per cent. of the hook-worms, whereas the fractions containing ascaridole, given in the same quantities, destroyed 81 per cent. of the worms. The effect on ascaridæ was the same with either fraction.

According to van der Wielen the action of the different fractions on isolated intestinal worms ought to be determined, in order to refute the opinion now prevailing that oils of higher specific gravity are to be preferred to those of lesser density. Furthermore only the innocuous lower-boiling fractions of the oil ought to be used as remedies. The supposition would be very natural that the chief component of the lower boiling fractions, *p*-cymene, possessed the vermifugal properties[6]).

In the meantime another publication by Henry and H. Paget[7]) has appeared, in which they experimentally refute van der Wielen's above opinion. The authors examined Hall and Hamilton's assertion (see above) that not the ascaridole but the lower-boiling

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[1]) Cf. also the article of Henry and Paget, mentioned before, and *Bericht* **1921**, 15. — [2]) *Journ. Americ. Pharm. Assoc.* 9 (1920), 127; *Bericht* **1920**, 61. We made the same observation many years ago. Cf. *Report* April **1908**, 169. Cf. also Gildemeister and Hoffmann, *The Volatile Oils,* 2nd edition, vol. II, p. 360. — [3]) This seems to be too hasty a conclusion. — [4]) *Journ. of Pharm. and Exp. Therap.* **11** (1918), 231. — [5]) *Gen. Tijdschr. voor Ned. Ind., Afl.* 1, *Deel* 61, **1921**. — [6]) Taking into consideration what other observers have stated, this judgment also seems a little hasty. — [7]) *Pharmaceutical Journ.* **107** (1921), 349. As per *Pharm. Ztg.* **67** (1922), 126.

fractions of the oil, the terpenes, are the efficacious constituents. They found that the vermifugal action was due exclusively to the ascaridole and not to the hydrocarbons. The products forming on decomposition of ascaridole in the heat were completely inefficacious.

E. K. Nelson[1] publishes a method which makes it possible to determine quickly the ascaridole content of wormwood oil. It is based upon the solubility of ascaridole to the extent of 98 per cent. in a mixture of 60 parts of glacial acetic acid and 40 parts of water. The wormseed oil terpenes are insoluble in such a mixture. The test is carried out as follows: — 10 cc. of chenopodium oil are vigorously shaken in a cassia flask with 60 per cent. acetic acid. Then acetic acid of the same strength is added up to the mark, when the ascaridole content can be calculated from the quantity of undissolved oil. The author found like that in five samples from 48 to 73 per cent. of ascaridole.

Ch. Sparhawk[2] gives an illustrated description of three varieties of American wormseed (*Chenopodium ambrosioides*, L., var. *anthelminticum*, Gray). The first, wild variety, a tangled mass of leaves, seeds, &c., does not produce much oil, although it feeds ravenously on the fertilizing material. A second, highly developed variety is distinguished by many seeds, with practically no leaves. This is the grade that produces the best oil, although the yield is not the largest. The third type, with stocky stem, plentiful leaves, and seeds on short stalks, gives the biggest returns, but the quality of the oil is not so good. Sparhawk adds that the seeds alone do not give any oil[3] but that the percentage of seeds seems to indicate the quality.

The superiority of chenopodium oil over thymol in the treatment of hook-worm disease is described in a report of the Uncinariasis Commission to the Orient[4]. Whereas there was failure to cure the patient in 23.6 cases out of a hundred treated with thymol, there were only 7.6 failures with chenopodium. Apart from the many advantages, which we have pointed out before[5] and the enumeration of which is therefore unnecessary, chenopodium oil has a disadvantage, according to the report in question, in that it often causes by-effects, such as dizziness, unsteadiness of gait, inability to rise, headache, &c. Certain purges intensified the toxic effects, thus giddiness and deafness were more marked among patients having castor oil than among those having magnesium sulphate.

W. Schüffner and H. Vervoort[6] communicate that in British East India and the U. S. A. too large doses (3 cc.) of American wormseed oil were frequently given. Toxic effects (vomiting, dizziness, deafness, &c.) were often the result, so that the oil nearly lost its good reputation in these countries. In the same degree as the doses were gradually reduced (down to 1.2 grams), the bad by-effects ceased. According to the authors the age of the oil seems to have an influence on both efficacity and poisonous nature. Cajus and Mhaskar[7] found that the ascaridole content went down from 70 to 56 per cent. in the course of one year. Wrench[8] reports that a chenopodium oil which, after having been stored for one year still contained 66 per cent. of ascaridole, had lost its original noxiousness, but nothing of its efficacity. If Wrench's observations are correct,

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[1] *Journ. Americ. Pharm. Assoc.* **10** (1921), 836. — [2] *Perfum. Record* **12** (1921), 388. — [3] Cf. Wirth's treatise (*Bericht* **1920**, 60). Wirth proved that the oil is contained only in the hairs on the seeds and the leaves. — [4] *Perfum. Record* **12** (1921), 57. — [5] Cf. *Report* **1919**, 113. — [6] *Mededeelingen van den burgerlijken geneeskundigen Dienst in Nederlandsch-Indië* **1921**, I, 29. — [7] *Indian Journ. of med. Research* **1920**. — [8] *Ibid.* **1918**.

oil that has been stored for some time would be preferable to the fresh product, as being less poisonous. — Schüffner and Vervoort recommend as a medium dosis three times 0.4 grams of chenopodium oil daily. Better results had been obtained with several small doses than by giving a larger quantity in one dosis. A laxative ought not to be given before, but after the cure. Anæmic persons should drink Karlsbad waters during the cure, which takes about five days. People suffering from kidney or liver complaints are very sensitive and should be treated with small doses only.

Chenopodium oil is said to have proved efficacious too as a remedy against tape-worms.

An article in the *Apothekerzeitung* also points out the danger of giving too large doses of American wormseed oil¹). According to H. Brüning a dosis of 0.2 cc. per kilo of weight was deadly for dogs, smaller doses caused paralysis, for instance of the respiratory organs. The oil can be given pure or in emulsions and is said not to have the disagreeable by-effects produced by santonin. — Children ought to have as many drops as they are years old, but not more than ten, to be given after a little breakfast. Two hours later castor oil or another mild aperient should be given. The author proposes to include the remedy in the new edition of the German Pharmacopœia and to fix the maximum doses.

The following cases show that it is not superfluous to call attention to the noxiousness of chenopodium oil when given in large doses: —

A child of two years, who had taken 8 grams of wormseed oil, meant for an older brother or sister, died in spite of all medical assistance²).

As per *The Perfumery and Essential Oil Record*³) oil of chenopodium has been the cause of a fatality at the Hospital for Tropical Diseases, Endsleigh Gardens, London, N.W.

Regarding the production of chenopodium oil in Java see p. 80 of this *Report*.

Pharmacopœias.

Italian Pharmacopœia.

(Farmacopea Ufficiale del Regno d'Italia, ed. IV.)

The third edition of the Italian pharmacopœia, in use since 1910, has now been succeeded by a new one, the paragraphs of which concerning our articles we wish to deal with in the customary manner. Unfortunately, not much favourable can be said about them. Indeed, we could confine ourselves to a mere reference to our criticism of the former edition of the pharmacopœia (*Report* April **1910**, 128) since the compilers deemed it unnecessary to do away with the numerous faults and mistakes of the third edition, and in the few cases where this was attempted it was performed rather unsatisfactorily. Here, the compiler of the paragraph ought to have realised that incorrect statements are of but little use in commercial intercourse, as they give rise to groundless objections and unnecessary correspondence. There was no difficulty in eliminating the existing errors, if one had taken pains to look out in the respective literature.

It may be taken for an effort to modernisation that with the essential oils notice has been taken of the direction of optical rotation, but since no limits have been

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¹) *Apoth. Ztg.* **36** (1921), 375. — ²) *Pharm. Ztg.* **66** (1921), 697. — ³) *Perfum. Record* **12** (1921), 185.

stipulated, this innovation is of hardly any use. In the subsequent discussion of the details, we have made up for this omission.

No new essential oil has been admitted; cajuput oil has been struck out.

In discussing the separate articles we follow the text of the pharmacopœia.

Anise Oil *(Essenza di anice).* — Colourless or yellowish; d_{20° 0.980 to 0.990; α_D to the left[1]); congeals on chilling to a crystalline mass which begins to melt at 15° and liquefies completely between 19 to 20°[2]); soluble in 2 to 3 vols. of 90 per cent. alcohol. Test for phenols with ferric chloride[3]).

[1]) The lævorotation amounts to —2°.

[2]) Solidification must often be brought about by inoculating the chilled oil with some solid anise oil or anethole. Good quality oil begins to melt again above 17°. In case of careless storing, or after repeated melting the solidification point decreases constantly and the density increases. Comp. *Report* October **1904**, 38.

[3]) This test is superfluous, since it traces a sophistication never observed with anise oil.

Cade Oil. — See Juniper Oil, empyreumatic.

Camphor *(Canfora).* — White, crystalline, translucent mass; d_{15° 0.993[1]); m.p. 179°[2]); burns with a sooty flame; volatile already at ordinary temperature; hardly soluble in water (1:1200), readily in alcohol, ether, chloroform, acetic acid, fatty and essential oils. 0.1 g camphor must volatilise without leaving a residue; test for chlorine.

Natural camphor is optically active, synthetic inactive[3]).

[1]) This statement is quite useless, the more so as nothing is stated as to how this constant is determined. The value given is but only an approximate one.

[2]) In the 3rd edition the melting point was correctly given as 175°.

[3]) Under certain conditions, also the synthetic preparation is active; comp. *Report* October **1910**, 197.

Cassia Oil. — See Cinnamon Oil.

Cedro Oil *(Essenza di cedro[1])).* — Greenish-yellow, the oil obtained by distillation being colourless[2]); d_{15° 0.857 to 0.861; α_D strongly to the right[3]); very sparingly soluble in water, soluble in about 5 parts of 90 per cent. alcohol[4]) and in every proportion in absolute alcohol.

[1]) Form the specific gravity required it follows that *lemon oil (essenza di limone)* is meant, since the various cedro oils (which are no articles of commerce) are partly heavier, partly lighter than stated above. Compare Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. III, p. 77.

[2]) Lemon oil is usually light yellow. Oils obtained by ordinary distillation are inferior and of no keeping quality.

[3]) The rotation amounts generally to +57 and +61°, oils occurring with higher or lower rotations. These data pertain to a temperature of 20°, this being important on account of the change of rotation with the temperature.

[4]) The solution, effected by 6 to 8 vols. of 90 per cent. alcohol, is often turbid due to the presence of mucous or vegetable wax-like substances.

Chamomile Oil *(Essenza di camomila comune).* — Blue, turning brown[1]) when exposed to the air, or when in contact with alcoholic soda solution. d_{15° 0.925 to 0.945; Roman chamomile Oil[2]) having d_{15° 0.905 to 0.915; soluble in 8 parts of 90 per cent. alcohol, opalescence occurring sometimes[3]); on chilling down to 0° it gets tough but does not solidify[4]).

[1]) Intermediately, the oil turns green.

[2]) It would have been better to quote this oil separately, as it behaves quite differently from ordinary chamomile oil. In discussing the other details of this paragraph, we take only the latter oil into consideration.

[3]) In consequence of its high content of paraffins, the oil gives but turbid mixtures with 90 per cent. alcohol.

[4]) This statement is incorrect, chamomile oil being, at 9°, a comparatively solid mass.

Cinnamon Oil (Cassia and Ceylon Cinnamon Oils) *(Essenza della cannella).* — Colourless or light yellow, turning gradually into yellow or brown[1]); soluble in 3 parts of 70 per cent. alcohol[2]); d_{15° with Ceylon oil 1.024 to 1.040; α_D to the left[3]); d_{15° with

Cassia oil 1.055 to 1.065[4]). Reactions with nitric acid and with ferric chloride; percentage of cinnamic aldehyde not below 70[5]).

[1]) Cassia oil is from the beginning dark yellow to brown; neither of the two cinnamon oils are colourless.

[2]) With cassia oil, the solution is in most cases not quite clear.

[3]) Up to —1°, rarely higher. With cassia oil, the rotation amounts up to —1° and +6°.

[4]) The upper limit is given too low, it must read 1.070.

[5]) This does not apply to either of the oils. With Ceylon cinnamon oil, the aldehyde content amounts to 65 to 76 per cent.; with cassia oil, the lowest value is at least 75 per cent.

Clove Oil *(Essenza di garofani).*—Yellowish, turning gradually brown when exposed to the air; d_{15° 1.045 to 1.070; soluble in 2 parts of 70 per cent. alcohol; eugenol percentage at least 85 when tested with 5 per cent. caustic potash solution[1]); identity reaction and test for absence of phenol[2]).

[1]) The amount of caustic solution required by the pharmacopœia is insufficient. This fact has equally been pointed out by V. Massera (*Riv. Ital. delle essenze e profumi* 3, Jan. 12, **1921**; acc. to *Chem. Zentralbl.* **1922**, II. 171) who suggests to shake, in a cassia flask, 10 cc. oil with 100 cc. 3 per cent. caustic soda solution.

[2]) Adulterations of clove oil with phenol have never been observed hitherto. A note on the rotation might have been useful, clove oil rotating to the left, up to —1° 35′.

Eucalyptole *(Eucaliptolo).* — Colourless; d_{15° 0.930[1]); b.p. 176 to 177°; solidifies, in a freezing mixture, to a crystalline mass which remelts at —1°[2]); identity reaction with bromine; when mixed with the same volume of carbon disulphide eucalyptole must yield a clear mixture (test for water); test for phenols with ferric chloride[3]).

[1]) The specific gravity ranges between 0.928 and 0.930.

[2]) Eucalyptole melts at about +1°. If necessary, congealing must be started by rubbing the glass walls with a glass rod.

[3]) This test is unnecessary, on the other hand, it might have been pointed out that eucalyptole must be inactive.

Eucalyptus Oil *(Essenza di eucalipto).* — Light yellow[1]), on exposure to the air it turns brown and resinifies; d_{15° 0.910 to 0.930; α_D faintly to the right[2]); soluble in 3 vols. of 70 per cent. alcohol; percentage of eucalyptole not below 70, tested by the resorcinol method[3]).

[1]) Eucalyptus oil is colourless, pale yellow, or pale greenish.

[2]) The rotation amounts up to +15°.

[3]) The pharmacopœia prescribes our *original* test of shaking 10 cc. oil with 90 cc. of a 50 per cent. resorcinol solution. Since sometimes too high figures are obtained hereby, we later on modified the method. Compare *Reports* April **1908**, 50 and October **1915**, 20.

Juniper berry Oil *(Essenza di ginepro).* — Colourless or faintly greenish yellow, thickening on exposure to the air and light and turning then more yellow; d_{15° 0.865 to 0.885[1]); soluble in 9 parts of 90 per cent. alcohol[2]) and in 1 part of carbon disulphide[3]).

[1]) The lower limit is given too high, it must read 0.860.

[2]) Only freshly-distilled oils answer this requirement; the solubility decreases rapidly.

[3]) A possible turbidity is caused by a slight content of water due to the preparation of the oil. Here, too, a reference might have been made to the optical rotation, the latter being to the left and amounting usually up to —13°, rarely higher.

Juniper Oil, empyreumatic (Cade Oil) *(Olio cadino).*— Dark brown; d_{15° 0.99 to 1.05; sparingly soluble in water to which it imparts an acid reaction; soluble in ether, chloroform, and absolute alcohol; miscible with carbon disulphide and benzine only with turbidity; about 65 per cent. of the oil must distil between 150 and 300°; identity reactions.

Lavender Oil *(Essenza di lavanda).* — Colourless[1]), faintly yellow or green; d_{15° 0.882 to 0.895; α_D to the left; soluble in 3 parts of 70 per cent. alcohol; percentage of linalyl acetate, at least 35; test for absence of citric ester[3]).

[1] Only the rectified oils are colourless, these, however, being of inferior quality. Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 434, footnote 2.

[2] The rotation ranges between —3 and —9°.

[3] This test should have been extended to other esters which may likewise be present besides ethyl citrate. Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 441 and *Bericht* (German) 1920, 39.

Menthol *(Mentolo)*.—Colourless prisms; m. p. 44°[1]); b. p. 212°[2]); nearly insoluble in water, most readily soluble in alcohol, ether, chloroform, and carbon disulphide, soluble in fats and paraffin oil; 0.1 g. menthol must not leave behind a weighable residue when evaporated on a water bath; test for absence of thymol[3]).

[1] A certain allowance must be granted, *i. e.*, 42 to 44°.

[2] Menthol boils under 753 mm. at 215°, the mercury thread being wholly surrounded by the vapours.

[3] Since mixtures of menthol and thymol are liquid this adulteration is highly improbable.

Methyl Salicylate *(Salicilate de metile)*.—Colourless; soluble in alcohol, ether, paraffin oil, fatty and essential oils; scarcely soluble in water: d_{15° 1.182 to 1.187[1]); b. p. 218 to 221°. On shaking with water the volume of the ester must not decrease to a noticeable extent (test for absence of methyl or ethyl alcohol); identity reaction with ferric chlorides.

[1] The limits are incorrect, the specific gravity ranging between 1.185 and 1.190 (15°).

Mustard Oil, natural and artificial *(Essenza di senape)*.—Colourless, afterwards yellowish with a tinge of red; b. p. 148°[1]); d_{15° with the artificial oil 1.020, with the natural oil 1.018 to 1.025[2]); $\alpha_D \pm 0°$; readily soluble in alcohol, ether, and carbon disulphide, sparingly soluble in water (1:1000); identity reactions; percentage of *iso*-thiocyanallyl, 94 to 99.

[1] This requirement must read correctly, mustard oil boils *for the greater part* between 147 and 153°.

[2] This statement is likewise incorrect; the specific gravity of the artificial oil is between 1.020 and 1.025, that of the natural oil between 1.014 and 1.025 (15°).

Orange Blossom Oil *(Essenza di fiori d'arancio amaro)*.—Yellow, turning reddish under the influence of air and light; blue fluorescence; d_{15° 0.870 to 0.880; α_D to the right[1]); soluble 1 to 2 parts of 90 per cent. alcohol; on adding more opalescence ensues[2]).

[1] French neroli oil, the chief commercial product, rotates between +1° 30′ and +9° 8′, Spanish oil between +9° 30′ and +29°, Italian oil between +2° 54′ and +56° 30′; the two last-named oils are, however, in all probability no pure distillates from the flowers of the bitter orange.

[2] This statement applies for 80 per cent. alcohol; in 90 per cent. alcohol, orange flower oil is clearly soluble in every proportion. After some time, however, slight opalescence sets in owing to a separation of paraffin.

Peppermint Oil *(Essenca di menta)*.—Colourless, straw-yellow, or greenish, on exposure to the air turning gradually yellow and viscous; d_{15° 0.890 to 0.920; d_{15° of the Italian oil 0.908 to 0.925; α_D strongly to the left[1]); English oil dissolves in 3 to 5 volumes of 70 per cent. alcohol, Italian oil gives with about 2 volumes sometimes a slightly opalescent solution which does not become clear on further dilution[2]); solidifying at —8 to —20° with separation of menthol, Italian oil does not solidify even at —17°; colour reaction with glacial acetic and nitric acids[3]); test with iodine for absence of turpentine oil[4]).

[1] The rotation ranges between —20 and —34°, with Italian oils between —2° 30′ and —26° 51′.

[2] American oils which, to judge from the specific gravity, are equally official, give generally a faint opalescence of the solution; with English oils this is sometimes likewise the case.

[3] We consider it decidedly a failure to comprise such a reaction (to which even otherwise normal English oils do not always answer) amongst the requirements of a pharmacopoeia. The quality of an oil musts never be judged by this reaction. It would have been far more correct to require a definite minimum content of menthol which with good commercial oils is not below 50 per cent.

[4] This test is entirely superfluous, quite obsolete, and absolutely useless, and ought to have been abandoned in the prior editions.

Rosemary Oil *(Essenza di rosmarino).*— Colourless or yellowish-green; d_{15° 0.90 to 0.92; soluble in 10 parts of 90 per cent. alcohol¹).

(1) Rosemary oil dissolves already in one-half volume of 90 per cent. alcohol.

Sandalwood Oil *(Essenza di sandalo).*— More or less yellow; d_{15° 0.975 to 0.985 (1); α_D to the left (2); soluble in 5 parts of 70 per cent. alcohol; santalol ($C_{15}H_{24}O$) content not below 90 per cent. (3).

(1) The lower limit should be 0.973.

(2) The angle of rotation lies between —16 and —20°.

(3) This minimum content does not agree with the statements given in the pharmacopœia as to the estimation of santalol which correspond to a content of 87.26 per cent.

Terpine Hydrate *(Terpina idrata).*— Lustrous, colourless and odourless prisms; on drying in a vacuum or above sulphuric acid it loses about 9.5 per cent. water; soluble in about 250 parts of cold, in 32 parts of boiling water, or in 10 parts alcohol, insoluble in light petroleum; the aqueous solution must show neutral reaction; terpine hydrate melts at 116°, terpine at 102° (1); on boiling the aqueous solution acidified with sulphuric acid a smell of hyacinths (2) is produced; 0.1 g. terpine hydrate must burn without leaving a residue.

(1) Terpine melts at 104 to 105°.

(2) In this reaction, terpineol is formed which, however, smells of lilac and not of hyacinth.

Thymol *(Timolo).*— Colourless, translucent crystals; m. p. 49 to 50° (1); b. p. 228 to 230° (2); sparingly soluble in water (about 1:1200), the aqueous solution must show neutral reaction; soluble in less than 1 part of alcohol, ether, acetic acid, chloroform, and fatty oils; soluble in 2 parts of 10 per cent. caustic soda solution; melted thymol floats on water, solid thymol drops down; 0.05 g. thymol, when heated on the water-bath, must volatilize completely; identity tests and test for absence of phenol.

(1) The m. p. lies between 50.5 and 51.5°.

(2) Thymol boils, under 753 mm. pressure, at 232°, the mercury thread being fully surrounded by the vapours.

Turpentine Oil *(Essenza di trementina).*— Colourless; boiling range, 155 to 162°; d_{15° 0.860 to 0.877; α_D to the right or the left according to the origin of the oil (1); perfectly volatile; hardly soluble in water, soluble in 12 parts 90 per cent. alcohol, 7 vols. 94 to 96 per cent. alcohol, in every proportion of absolute alcohol, ether, chloroform, carbon disulphide, fatty and essential oils (2); resinifies when exposed to the air; neutral reaction; when kept in a bottle but partly filled the oil turns yellow and shows acid reaction.

For certain purposes, the crude oil is admitted, which is colourless or faintly yellow and leaves on evaporation a residue of 2 per cent. (3).

In addition, old, so-called ozonised oil must be kept for use, which colours blue a paste of starch and potassium iodide.

(1) The rotation ranges between +41° and —35°.

(2) Possible turbidity is caused by a small amount of water in the oil owing to the distillation process. On addition of a desiccating substance, *e. g.*, sodium sulphate, such turbidities disappear instantaneously.

(3) This evaporation must be performed with special precautions, as otherwise too high values may result. Compare Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 20.

Chemical Preparations and Drugs.

Benzaldehyde. — In our last *Bericht*[1] we accurately described our method of quantitative determination of chlorine in benzaldehyde. The apparatus then shown in the picture, and supplied by the Leipzig firm of F. Hugershoff, has meanwhile been slightly modified.

Both the U-tubes serving as absorbing vessels have been provided with a short pipe each which can be closed by means of a piece of rubber tubing and a pinchcock, so that the absorbing liquid can now be more easily removed. Furthermore, the glass tube connection the two U-tubes has been provided with a small bulb, as sometimes the liquid of the first U-tube passed over into the second.

In addition we would mention the fact that the air in the laboratories is liable to contain hydrochloric acid gas and that then even passing it through dilute silver nitrate solution may not free it entirely from chlorine. We therefore connect the apparatus with the fresh air outside by means of a glass tube passed through a small opening in a window.

As previously mentioned[1] we consider the indication of "benzaldehyde, technically tree from chlorine" as a nuisance, liable to cause confusion to the detriment of the honest dealer. Our opinion has since been confirmed, for its is almost incredible what stuff is frequently offered under above designation. There are products of all shades, from a slight to the most pronounced chlorine reaction, and it is only a matter of how elastic the conscience of the supplier may be for terming the product "technically" or, as it is now called, "commercially free from chlorine".

Out of the many samples which have been examined in our analytical laboratories we would only mention one, just to show what amount of cheek some suppliers have. The constants were as follows: d_{15° 1.0633, $\alpha_D + 0^\circ 6'$, n_{D20° 1.54054, completely insoluble even in 10 volumes of 50 per cent. alcohol, acid v. 12.5 = 2.7 per cent. benzoic acid, chlorine reaction: extraordinarily strong. This shows that the article was absolutely unsatisfactory, not a single one of the constants coming up to the requirements for benzaldehyde. It is even too bad for a crude product, as results from the defective solubility and the excessive specific gravity, which latter cannot be explained by an excess of benzoic acid, into which benzaldehyde may be converted by oxidation. These two properties referred to induced us to examine the sample a little more closely, as far as the small quantity permitted. It resulted that the product contained only 68 per cent. of benzaldehyde. The quantity at our disposal was not large enough for further investigation regarding the admixtures, &c.

W. von Rechenberg[2] prefers Beilstein's copper oxide test for chlorine in benzaldehyde to the well-known combustion method. After comparative tests, he ascribes more exact results to the former.

We have stated on previous occasions[3] that, in our opinion, the combustion method is decidedly more accurate and reliable than the copper oxide test, and we

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[1] *Bericht* (German) **1921**, 56. — [2] *Chem.-Ztg.* **45** (1921), 627. — [3] *Report* April **1912**, 151.

still adhere to this standpoint. We consider Beilsteins's test as useful only for general guidance, and it seems risky to us to deduce binding conclusions from it in all the cases, as owing to the perceptible volatility of the copper benzoate the flame may be coloured green by the benzoic acid, which would lead to erroneous conclusions[1]). We would therefore recommend caution when judging benzaldehyde by the result of the copper oxide test.

As to catalytic reduction of benzaldehyde with copper, and the pyrogenous decomposition of benzaldehyde, see pages 131 and 146 of this *Report*.

Benzylalcohol. — According to D. J. Macht and A. T. Shohl[2]) solutions of benzylalcohol keep their anæsthetic qualities unchanged when kept in ampoules of unattackable glass, and their hydrogen ion concentration varies but very showly. On the other hand, in glass which gives off alkali the solutions loss their anæsthetic power quickly and show alkaline reaction in the course of several months.

J. Messner[3]) gives the following explanation for the decomposition of benzylalcohol which is said to pass off also in neutral or feebly acid (acetic or hydrochloric acid) solution: — Apparently, reduction as well as oxidation takes place simultaneously, one molecule of the alcohol losing oxygen with formation of toluene, a second molecule absorbing the oxygen liberated with formation of benzaldehyde and water: — $2C_6H_5CH_2CH = C_6H_5CH_3 + C_6H_5CHO + H_2O$. This reaction may be accelerated by action of light, or owing to the presence of organic or inorganic impurities in the water or the benzylalcohol. The latter can even be its own catalyst, as has been proved by Jacobson. Messner strongly disapproves that aqueous solutions of benzalcohol, which decompose easily, be traded in ampoule fillings.

By heating benzylalcohol, in xylene solution, with barium sulphate + palladium K. W. Rosenmund and F. Heise[4]) obtained 5 per cent. benzaldehyde, 12 per cent. benzyl ether, 50 per cent. benzylalcohol, and 20 per cent. undistillable residue. Pure barium sulphate was of no influence on the alcohol.

The action of the benzyl esters on the human or the animal organism may be attributed either to the unchanged benzyl ester molecule or to the benzylalcohol formed in the body by hydrolysis of the ester. The fact that benzyl acetate and benzoate are excreted as hippuric acid and that benzylalcohol has a relaxing effect on the unstriped muscle seems to indicate that the effect is due to the hydrolysis of the esters[5]). Hence, it would be rather probable that the therapeutic effects would be proportional to the rates of hydrolysis of the esters. This possibility induced E. H. Volwiler and E. B. Vliet[6]) to investigate the chemical part of the problem and to compare the rates of hydrolysis of a number of benzyl ethers. Their experiments, which were conducted according to the directions of Bischoff and Hedenström[7]), proved that the rates of hydrolysis of the esters, under identical conditions, increase in the following order: — salicylate, benzoate, stearate, cinnamate, acetate, succinate, and fumarate. In benzyl acetylsalicylate, the rate of hydrolysis is of the same order as in benzyl salicylate.

The authors give a description of the methods employed for the preparation of some of the esters. The preparations had the following constants: — fumarate, m. p. 58.5

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[1]) Cf. Kunz-Krause, *Apotheker-Ztg.* **30** (1915), 141. *Report* October **1915**, 56. — [2]) *Journ. of Pharm. and exper. Therap.* **16** (1920), 61. As per *Therap. Halbmonatsh.* **35** (1921), 216. — [3]) *Pharm. Zentralh.* **63** (1922), 1. — [4]) *Berl. Berichte* **54** (1921), 2042. — [5]) Macht, *Journ. Pharmacol.* **11** (1918), 263. — [6]) *Journ. Amer. chem. Soc.* **43** (1921), 1672. — [7]) *Berl. Ber.* **35** (1902), 3433.

to 59,5°, b. p. 210 to 211° (5 mm.); salicylate, b. p. 170 to 175° (7 mm.); cinnamate, m. p. 33 to 34°, b. p. 228 to 230° (22 mm.); acetylsalicylate, m. p. 25.5 to 26.0°, b. p. 197 to 200° (7 mm.).

Benzyl Benzoate. — E. C. Mason and E. C. Pieck[1]) did not notice any change worth mentioning in the respiration of dogs after an intravenous injection of 2 cc. of 10 per cent. benzyl benzoate solution; breathing became flatter after an injection of 4 cc., the blood pressure decreased and the contractions of the pylorus became feebler. The latter ceased altogether after an injection of 6 cc. (the breathing stopped at the same time, causing death). The solution had only a slight effect on the tension of the small intestine; lage doses may cause hearth failure. The action on the uterus was very feeble, the increase of the pressure in the artery of the lungs inconsiderable, whereas no extension of the bronchioles could be proved.

According to E. A. Heller and E. Steinfield[2]) daily injections, repeated for four days, of 1 cc. each and one injection of 1.5, 2 and 2.5 cc., respectively, of benzyl benzoate per kilo of weight had no effect on the number of white corpuscles in rabbits. After larger doses the animals became sleepy and faint, one of them died.

Bromostyrene. — Theoretically, three monobromostyrenes substituted in the side-chain are possible, *i. e.*, the two stereoisomerides with the formula $\mathrm{Ph\cdot CH:CHBr}$ and the body $\mathrm{Ph\cdot CBr:CH_2}$. Two isomerides are hitherto known, namely one ω-bromostyrene $\mathrm{Ph\cdot CH:CHBr}$ (A) and the α-bromostyrene $\mathrm{Ph\cdot CBr:CH_2}$ (B). Ch. Dufraisse[3]) succeeded in obtaining the third isomeride, the other ω-bromostyrene (C), from bromobenzalacetophenone and powdered caustic soda: m. p. —8 to —7°; b. p. 71° (6 to 7 mm.); d_{20° 1.426; $n_{D22.5^\circ}$ 1.5990. Phenylacetylene resulted as by-product. Furthermore, the author obtained, by heating sodium dibromohydrocinnamate with sodium carbonate, according to Nef[4]), the well-known ω-bromostyrene (m. p. + 6 to 7°[5]); b. p. 107° (22 to 23 mm.); d_{20° 1.422; $n_{D20.5^\circ}$ 1.6094), and from phenylacetylene and hydrogen bromide, α-bromostyrene, m. p. —43°; b. p. 71° (7 to 8 mm.); d_{20° 1.406; $n_{D19.5^\circ}$ 1.5881.

With alcoholic potash solution the three bromostyrenes yield phenylacetylene. The bodies A and C, on treatment with bromine, gave rise to identical tribromostyrenes $\mathrm{Ph\cdot CHBr\cdot CHBr_2}$, m. p. 37 to 38°; thus the constitution of the three bromostyrenes as given above is proved to be correct.

The two geometrical isomerides of the m. p. + 6 to 7° and —8 to —7°, according to observations by the same author[6]), undergo most readily a mutual but partial rearrangement under the influence of sun-light. Strangely, the stable form (m. p. + 7°) obtains equilibrium sooner than the other modification. The mixture of the isomerides, when equilibrium is reached, melts at + 2° and shows the same odour as the stable form.

On exposure to the air, α-bromostyrene is readily oxidised to bromoacetophenone. Since freshly-distilled α-bromostyrene shows no irritating action on the mucous membranes, Dufraisse[7]) is of opinion that the irritation caused by older preparations must be ascribed to the presence of bromoacetophenone.

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[1]) *Journ. of Laborat. and Clin. Med.* 6 (1920), 62. As per *Chem. Zentralbl.* **1921**, III. 495. — [2]) *New York med. Journ.* **112** (1920), 160. As per *Chem. Zentralbl.* **1921**, I. 507. — [3]) *Compt. rend.* **171** (1920), 960. — [4]) *Liebig's Annalen* **308** (1899), 267. — [5]) With our own preparations we observed: — sol. p. ± 0 to 2.5°; the m. p. stated above must therefore be regarded with some suspicion. — [6]) *Compt. rend.* **172** (1920), 67. — [7]) *Ibidem* **172** (1921), 162.

Camphor. — D. A. Wallace and S. B. Plumer1) determined the amount of camphor in camphorated oils by heating the solution in cotton-seed oil for three hours, that in pea-nut or olive oils for four hours and that in sesame oil for five hours up to 120° and calculated the camphor content from the loss in weight. Camphorated oils are oxidized on heating and increase in weight. This increase in weight, which has been determined by the authors in certain cases, has to be taken into account when calculating the camphor content.

The authors further recommend the already known method2) of determining the the camphor content in camphorated oils by means of the optical rotation.

Castoreum. — At the annual auction in London, the Hudson Bay Company offered in December 1921 2649 lbs. of Canadian castoreum, of which 575 lbs. were sold. Of the Oregon quality 2932 lbs. were available, of which 1170 lbs. were disposed of3).

Coumarin. — According to a process invented by W. Ponndorf4) coumarins are obtained by condensing phenols or phenol ethers with fumaric or maleic acids under the influence of condensing agents such as zinc chloride, or aqueous or alcoholic 73 per cent. sulphuric acid, at a temperature not below 120°. The condensation of fumaric acid with phenols passes off by union of a hydrogen atom in *ortho* position of the phenol with one of the two COOH-groups of the acid, with formation of formic acid, and by ring-formation of coumarin from the resulting coumaric acid.

T. Yanagisawa and H. Kondo5), in preparing coumarin, make use of iodine as catalyst, and obtained, when boiling salicylic aldehyde, acetic anhydride, and sodium acetate for four hours in an oil both, a yield of 70 per cent. crude coumarin.

G. C. Bailey and F. Boettner6), when endeavouring to prepare methylcoumarin from malic acid and *m*-cresol, found the method devised by Fries and Klostermann7) to be the most successful one. They obtained the highest yield (54 per cent.) of methylcumarin when malic acid was added slowly to a the mixture of *m*-cresol and sulphuric acid heated to 135°, the reaction product then poured on ice, and the precipitate formed taken up in 50 per cent. alcohol and crystallised from this solvent. A *m*-cresol of 84 per cent. yielded about 40 per cent. of methylcoumarin.

Toxicity tests carried out with mice proved methylcoumarin to be not more than one-tenth as toxic as coumarin. As to the perfume value, dilute solutions of methylcoumarin were said to be of almost the same odour as those of natural coumarin. The odour of the dry crystals, however, was considerably less intense than with natural or synthetic coumarin.

Eucalyptole. — The cresineol method for the determination of cineole devised by T. Tusting Cocking8) gives, according to recent statements9) of the author, satisfactory results if the amount of cineole present in the sample reaches 45 per cent. and upwards. When the amount of cineole present falls below 45 per cent. the method must be modified insofar that a certain amount of pure cineole, or an equivalent amount of

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1) *Americ. Pharm. Journ.* **93** (1921), 600. — 2) Cf. *Reports* April **1915**, 73; **1918**, 92. Some angles of rotation are given for the oils mentioned, with and without camphor. — 3) *Oil, Paint and Drug Reporter* **101** (1922), No. 1, p. 32. — 4) Germ. Pat. 338737, published July 4, **1921**; *Chem. Zentralbl.* **1921**, IV. 1224. — 5) *Journ. pharm. Soc. Japan* **1921**, no. 472; *Chem. Zentralbl.* **1921**, III. 958. — 6) *Journ. ind. eng. Chem.* **13** (1921), 905. — 7) Cf. *Report* October **1906**, 96. — 8) Comp. *Bericht* (German) **1921**, 65. — 9) *Perfum. Record* **12** (1921, 339.

pure cresineol is added to the oil before carrying out the determination. The result is calculated by means of a table, with due regard to the cineole or cresineol added.

According to this modified method the author tested a series of oils with low cineole content, with the following results: —

	Percentage esters	Percentage cineole
Lavender oils, French . . .	29 to 52.7	18.0 to 22.6
„ „ English . . .	6.2 „ 10.7	23.6 „ 27.4
Spike oils	2.3 „ 3.9	33.2 „ 39.0
Rosemary oils, French . . .	3.1 and 4.1	23.2 and 25.4
„ oil, Spanish . . .	2.5	19.4

We abstain from discussing the correctness of these figures, yet we find the quantity of cineole found by Cocking in the French lavender oils remarkably high. According to our own observations¹), French lavender oils contain only very small amounts of cineole, and we come to the conclusion that Cocking must have dealt with adulterated, or highly impure oils. Should this not be the case, the results would certainly not speak in favour of the cresineol method, which, too, was originally devised for different purposes. In such a case, the statements concerning the cineole content of the other oils would have to be regarded with some doubts.

Gum Benjamin. — A. Mayrhofer²) examined a gum benjamin offered by a Vienna firm as Palembang benzoin and sent in tins of 15 kilos. The drug which ought to alter quickly its appearance when the pieces are broken and left in contact with the air, consisted of reddish-gray to gray-brown pieces which easily crumbled and showed on some larger surfaces the impression of white pieces of tissue. The neighbouring pieces of gum were gray or blackish. The main part of the substance was composed of pieces of wood, held together by a whitish or brownish-red, glossy mass. After exhaustive extraction with alcohol there was a residue of 52 to 68 per cent. No cinnamic acid was present (test with potassium permanganate). As to benzoic acid, 3.1 per cent. = 9 per cent. of the part soluble in alcohol, were obtained. The alcoholic extract had the following constants: acid v. 99.9 (determined indirectly), saponification v. 198.1 (determined in the cold). The microscopic examination of the pieces of bark showed that they originated from a Styracea.

The available data were therefore not sufficient to characterize the drug as Palembang benzoin, especially because the mother plant and origin of this commodity are not known well enough so far³). Nevertheless the article is said to have a certain value, as it may be useful, for instance, for preparing benzoin tincture.

Heliotropin. — The oxidation of *iso*safrole to heliotropin is considerably favoured by the addition of amino-carboxylic acids. On the strength of this fact C. Sievers and L. Givaudan & Co.⁴) publish a process, consisting in that 120 parts of *iso*safrole are oxidized at a medium temperature with a solution of either sodium bichromate

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¹) Comp. *Report* October 1893, 27. For safety's sake, we endeavoured to prove or determine, with four lavender oils of warranted purity, the cineole present and arrived at the result, in accord with our former experiences, that lavender oil contains but so little cineole, that the proof of its presence causes some difficulty. There is absolutely no possibility that pure lavender oils contain such an amount of cineole as stated by Cocking. — ²) *Apotheker Ztg.* 36 (1921), 821. — ³) According to Lüdy and Tschirch Palembang benzoin is exported from Palembang in Sumatra; Dieterich mentions as mother-plant a *Styracea* of Further India, about which nothing definite is known. — ⁴) Swiss Pat. 91087, Oct. 17, 1921. Addn. to 89053. Cf. p. 99 of this *Report*.

(240:1000) or chromic acid, in the presence of 10 parts of *p*-amino-benzoic acid, dissolved in 480 parts of 50 per cent. sulphuric acid. By way of the bisulphite compound one obtains 15 parts of unaltered *iso*safrole and 90 parts of heliotropin.

Menthol. — The list of articles which the Board of Trade considered dutiable under the Safeguarding of Industries Act includes menthol. We do not know what prompted the competent authorities to take this remarkable step, as an article is concerned which cannot possibly be made in England. Anyway this proceeding has roused a storm of criticism in the affected quarters in England[1]), so that the Board of Trade tried to get out of all difficulties by adding the letter "R" to menthol, which signifies that the chemical indicated is included only when it is "pure", "puriss.", "extra pure", "B. P.", &c. In criticizing this measure the *Chemist and Druggist* gives vent to the following opinion: "There is no specially purified menthol obtainable in commerce, except as a laboratory curiosity, and then it has no superiority over ordinary menthol." If the author knew that purified, *i. e.* recrystallized menthol is sold in ton lots on the continent and that, contrary to what may be the case in England, Germany and a good many other European countries use no other menthol at all for pharmaceutical purposes, he would surely have given a different verdict.

Further communications on menthol are to be found under the heading of Japanese Peppermint Oil, page 58 of this *Report.*

Musk. — Chungking is the chief port of original export for musk, which is brought into Szechwan from Tibet, says Consul P. R. Josselyn, Chungking[2]). During the ten years from 1893 to 1902 the average yearly export through the Maritime Customs at Chungking was 3971 pounds, while during 1918 the amount exported was only 948 pounds. This decline was partly due to the war; but for the last 15 years there has been a steady decline, which would indicate that the musk deer is no longer as plentiful or as easily caught as formerly[3]). Probably considerably less than one-half of the musk that comes into China from Tibet is exported abroad. The remainder is used locally by the Chinese medicine shops and as a perfume.

Before the war France took approximately 50 per cent. of the export, the United States being second, taking about 20 per cent. During the five years from 1910 to 1914 the average yearly export to the United States from all China was 406 pounds, valued at 120284 Haikwan taels[4]). During the three years 1915 to 1917, inclusive, it increased to 613 pounds, valued at 195087 Haikwan taels.

Musk, artificial. — According to A. Reclaire[5]) a "new brand of musk", received from France, contained no less than 82 per cent. acetanilide. For the quantitative determination of this well-known adulterant of artificial musk the author proceeded as follows, basing his method on the prescriptions given by A. Seidel[6]) and J. C. Tonus[7]): —

The acetanilide is decomposed by boiling it with 20 per cent. hydrochloric acid. The aniline formed is converted into tribromo-aniline by means of an excess of potassium bromide-bromate solution of known strength. After having added some potassium iodide solution, the excess of bromine is titrated back with sodium thiosulphate solution, when the content of aniline (acetanilide) can be calculated from

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[1]) *Chemist and Druggist* **95** (1921), 875. — [2]) *Americ. Perfumer* **16** (1921), 106. — [3]) Cf. *Bericht* (German) **1920**, 72. — [4]) As to the altered value of the Haikwan tael see *Bericht* (German) **1920**, 73. — [5]) *Perfum. Record* **12** (1921), 280. — [6]) *Journ. Americ. chem. Soc.* **29** (1907), 1091. — [7]) *Physisch-chemisch onderzoek van verbindingen, gevormd uit een amine en een organisch zuur* (Leiden **1918**).

the difference. This method is said to be sufficiently accurate for technical purposes (difference 0.4 to 0.6 per cent.).

O. Wichmann[1]) examined trinitro*iso*butyltoluene and trinitrobutylxylene as to their pharmacodynamic action. In the human or animal organism, by oxidation of the CH_3 group, the trinitrobutyltoluene splits off water which joins the butyl group. In this way tertiary butyl alcohol is formed in addition to *m*-trinitrobenzoic acid. The latter combines with glycocol, thus forming *m*-trinitrohippuric acid which is secreted with the urine. The tertiary butyl alcohol has the capacity of combining in the animal organism with glycuronic acid which also leaves the body with the urine. The human organism secretes the tertiary butyl alcohol through the respiration process.

In a closed room, insects (gnats and flies) were killed by the effect of artificial musk.

A subcutaneous injection of 0.05 to 0.1 gram of trinitrobutyltoluene dissolved in oil caused the death of cold-blooded animals (frogs) after four hours.

Warm-blooded animals were not affected by up to 1 gram taken internally. After a subcutaneous injection of 0.2 gram dissolved in oil an increase of the reflex movements was noticed in guinea-pigs; 0.4 gram caused death within 12 hours after previous signs of paralysis.

Doses up to 1 gram, internally, had no effect on human beings; but it is to be supposed that larger quantities injected subcutaneously must act as poison on the human organism.

A therapeutical use of trinitrobutyltoluene and trinitrobutylxylene is not very likely to come into consideration.

Myrtole. — The myrtle oil fraction boiling between 160 and 180° is used for inhaling under the name of myrtole. One of its essential components, which causes perhaps its praised antizymotic and desodorizing effect, is eucalyptole. This consideration apparently induced the supplier of a so-called myrtole, submitted to us for inspection, to give eucalyptole instead, a proceeding requiring a rather elastic conscience.

The sample behaved as follows: — d_{15° 0.9294, $\alpha_D \pm 0^\circ$, n_{D20° 1.45802, solidification point $+0.2^\circ$, soluble in 4 volumes and more of 60 per cent. alcohol. These constants tally completely with those of eucalyptole (d_{15° 0.928 to 0.950, $\alpha_D \pm 0^\circ$, n_{D20° 1.454 to 1.459, solidification point between 0 and $+1^\circ$, soluble in 4 volumes and more of 60 per cent. alcohol, whereas those of myrtole are entirely different, as is shown by the following figures established for myrtole of our own distillation: — d_{15° 0.884 to 0.904, $\alpha_D + 15$ to $+24^\circ$, n_{D20° 1.462 to 1.463, soluble in 0.5 volume and more of 90 per cent. alcohol, sometimes already in 80 per cent. alcohol (1 to 2 volumes).

The difference in price between myrtole and eucalyptole is so considerable, that above supplier's tactics paid well, even if he sold his "myrtole" very cheap.

Nitrobenzene. — We mentioned in our last *Bericht*[2]) that freshly marked linen caused symptoms of poisoning in babies. We are now told[3]) that they were not due to nitrobenzene, but to aniline.

In two cases of acute poisoning with nitrobenzene, due to "Jamaica gingers" containing this body, R. F. Loeb, A. V. Bock and R. Fitz[4]) examined the blood. Methæmoglobin was not present; the oxyhæmoglobin in the arterial blood was reduced to 6.2

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[1]) *Dissertation*, Bonn **1921**. As per *Apotheker-Ztg.* **36** (1921), 510. — [2]) *Bericht* (German) **1921**, 67. — [3]) *Deutsche med. Wochenschr.* **47** (1921), 1526. As per *Chem. Zentralbl.* **1922**, I, 480. — [4]) *Americ. Journ. of the Med. Sciences* **161** (1921), 539. As per *Chem. Zentralbl.* **1921**, III, 968.

and 4.8 per cent., the capacity of binding oxygen to 8.9 and 6.2 per cent., respectively. There was moderate leucocytose and, for six hours, anuria. In the urine *p*-aminophenol was present.

A further case of poisoning mentioned was brought about by resorption through the skin (the garments had been soiled with oil containing nitrobenzene).

As to the detection of nitrobenzene in bitter almond oil, see page 6 of this *Report.*

Peru Balsam. — A balsam of Peru, sent us for examination, was greatly adulterated or rather resulted to be a composition, but was termed genuine by the supplier, who refused to take it back, in spite of the repeated reclamations of the buyer. As the supplier was a large concern and in a position, no doubt, to have the article properly examined, this case is a perfect riddle for us. If one had taken the trouble to look into the matter, the determination of the specific gravity would have revealed already that there was something the matter.

Said balsam behaved as follows: — d_{15° 1.1387, cinnamein content 63.6 per cent., ester v. of the cinnamein 225.4, nitric acid test = bluish green colouring. There could not be any question of a pure, genuine balsam. Its specific gravity and the ester v. of the cinnamein were too low; besides, the cinnamein differed from the normal product in that it was not liquid at room-temperature, but semi-solid. The nitric acid test, leading to a golden yellow colouring in the case of genuine balsam of Peru, also indicated adulteration.

For any expert the stuff would have been suspicious on account of its odour and abnormally light colour. It is therefore remarkable, that the supplying concern in question did not notice anything. Needless to say that such a concoction does not answer the requirements of the pharmacopœia.

Peru Balsam, artificial. — We have taken up the manufacture and are pleased to state that our product meets with increasing popularity.

Bark of Rhamnus Frangula. — Through steam distillation of the bark of *Rhamnus Frangula,* O. A. Oesterle[1]) obtained 0.05 to 0.1 per cent. of a crystalline substance of strongly fusty smell, which had probably formed only during the distillation. The product contained, apart from dark coloured impurities, small quantities of a white crystalline body, insoluble in soda solution; a compound precipitated in the form of a jelly from hot soda solution; a body soluble in soda lye, crystallizing from water in radiate form, and a compound insoluble in soda lye, crystallizing from alcohol in the shape of brownish yellow scales. This inodorous and tasteless substance had the empiric formula $C_{15}H_{12}O_4$, m. p. between 100 and 101°.

Resin of a Peruvian Styracea. — E. Maldonado[1]) examined a resinous substance, known in the Province of Cuzco (Peru) by the name of *incienso macho* and frequently used for incense, perfumery and medical purposes. The drug comes probably from a variety of *Styrax* (*Styrax ovatum,* A. DC., occurs in the valleys of Cuzco, Umbara Valley) and forms irregular, hard, reddish-black or black masses. They are covered with a greenish dust and taste aromatic at first, then sharp. The fractured surface exhibits a brilliant, vitreous, yellow colour. The odours recalls that of vanilla. The

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[1]) *Bol. Farm. de Lima* of June 30th, 1920. As per *Chemist and Druggist* 95 (1921), 207.

author prepared from the drug a gum, an oxydase, vanillin, a small quantity of aromatic esters, and 5 per cent. of benzoic acid.

Thymol. — The Badische Anilin- und Sodafabrik in Ludwigshafen publish a method of preparing thymol from *m*-cresol[1]. The *m*-cresol is sulphonated, and the resulting *m*-cresol-sulphonic acid treated with *iso*propyl alcohol and sulphuric acid (preferably concentrated) in the warmth. The sulpho-group is split off the mass at a temperature of from 120 to 125°, the thymol being distilled off simultaneously. The oil thus obtained, which is almost completely soluble in dilute soda lye, is treated in the usual way and subjected to fractionated distillation. The first runnings contain the unaltered cresol, then the thymol passes over, whereas the last fraction contains probably an isomeride of thymol, crystallizing from benzene in large crystals (m. p. 114 to 115°).

The preparation of thymol from cymene has repeatedly been patented already[2]. R. M. Cole[3] suggests as a further improvement the electrolytic reduction of nitrocymene and the subsequent diazotisation and reduction of the 1-methyl-2-amino-4-*iso*propyl-5-hydroxybenzene. The diazo-group is then replaced with hydrogen in the usual way.

Nothing is mentioned in the discussions as to the yield.

By condensation of one molecule of salicylaldehyde and two molecules of thymol in the presence of some dilute sulphuric acid, F. Lavilla Llorens[4] obtained hydroxyphenyldithymylmethane $OH \cdot C_6H_4 \cdot CH : (C_6H_2 \cdot CH_3 \cdot OH \cdot C_3H_7)_2$, m. p. 185°; methylether, m. p. 137 to 138°; ethylether, m. p. 77 to 78°. In these compounds all the three hydroxyl-groups reacted. Tribromo derivative, m. p. 170°; iodine derivative, m. p. 111°. By double interaction of the alkali derivatives with metal salts the lead, copper and iron compounds were obtained.

According to R. Maire[5] the following three species of *Ptychotis* occur in North Africa: — 1. *Ptychotis Ammi,* L. = *Sison Ammi,* L. = *Seseli ammoïdes,* L. = *Ptychotis ammoïdes,* Koch, a small annual plant occurring so abundantly in fallow ground that one might think it was cultivated. This umbelliferous plant, found in all southern Europe, is easily recognized by its smooth, naked stems and leaves, its petiolate pinnules and its white inflorescences provided with dimorphous bracts but without any involucre. 2. *Ptychotis trachysperma,* Boiss. = *P. aspera,* Pomel., is distinguished from the former by its wrinkled fruits and its spatulate bracts. It occurs in western North Africa and in Spain. 3. *Ptychotis atlantica,* Coss., a perennial flowering late and occurring frequently in the higher mountains (Tell Mountains in the departments of Algiers and Constantine; Aurès Mountains). All the parts of these plants smell strongly of thymol, especially the fruits, and might perhaps be used for the manufacture of this phenol.

Brocq-Rousseu[6] mentions that horses can stand internal doses of 0.22 to 0.25 gram of thymol per kilo. From 0.20 gram upwards symptoms of paralysis occur. The symptoms of poisoning are faintness, ataxy, fall of temperature and often paralysis of

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[1] *D.R.P.* 350809 of July 4th, 1920. — [2] Cf. *Berichte* (German) 1920, 77; 1921, 74. — [3] *Perfum. Record* 12 (1921), 281. *Chem. Zentralbl.* 1921, IV. 513. — [4] *Ann. Soc. Espanola Fis. Quim.* [2] 18 (1920), 139. As per *Chem. Zentralbl.* 1921, III. 785. — [5] *Parfum. moderne* 14 (1921), 79. — [6] *Compt. rend. soc. de biologie* 84 (1921), 257. As per *Chem. Zentralbl.* 1921, III. 125.

the hind-legs. If the thymol stays for any length of time in the stomach or in the intestins, it irritates the mucous membranes. Aristol (dithymoldiiodide) is soluble in water and in the gastric juice.

Vanillin. H. C. Sievers and L. Givaudan & Co.[1]) publish a method of preparing vanillin from acetyl*iso*eugenol by oxidation with sodium bichromate or chromic acid, in the presence of amino-carboxylic acids. The addition of 1.5 to 2 per cent. of such a amino-carboxylic acids as catalyst, for instance *p*-amino-benzoic acid, has a favourable influence on the oxidation and on the yield of vanillin. One proceeds as follows: 120 parts of *iso*eugenol are distributed in 1240 parts of a sodium bichromate solution (250 parts in 1000 parts of water); under continuous stirring at a temperature of 80°, a solution of 1.5 to 2 parts of *p*-aminobenzoic acid in 500 parts of 50 per cent. sulphuric acid is allowed to flow in. As soon as the oxidation is completed the acetylvanillin formed is extracted with a solvent and the vanillin obtained by way of the bisulphite compound. One obtains 12 parts of unaltered acet*iso*eugenol and 68 parts of vanillin.

The yield is the same if the amino-carboxylic acids are replaced by aromatic amino-aldehydes, such as *p*-amino-benzaldehyde[2]).

As to the manufacture of vanillin from guayacol and formaldehyde, see page 143 of this *Report*.

Two samples of vanillin tested in our laboratories were grossly adulterated; one containing about 55 per cent. of antifebrin, the other 75 per cent. of benzoic acid. The adulterants influenced the melting point considerably, of course, for the preparation containing antifebrin melted already between 64 and 68° (instead of at 82°), whereas the other began to sinter at 68° and was completely melted only at 110°.

The antifebrin was separated off by shaking the product, dissolved in ether, with soda lye, when only the vanillin is taken up by the soda lye. The antifebrin remained in the ether and was obtained by evaporating the solvent, it was recognized by its melting point (113 to 114°) and by its *iso*nitril reaction.

The benzoic acid was separated in a similar way, only that in this case the vanillin was removed from the ethereal by shaking it with bisulphite lye. The residue obtained on evaporation of the ether melted at 121° and could be identified as benzoic acid also by its other properties.

Taking into consideration the difference of price between vanillin and these two adulterants, one easily understands that the buyers of the article will have paid far too much for it in spite of the apparently low price.

The methods of vanillin determination in vanilla extracts[3]), according to which lead acetate is added to the dealcoholized extract and the aldehyde is the determined by weight, often lead to inexact results. Either the vanillin obtained is not quite pure and the figures are too high, or the purification causes losses. The method indicated by Hiltner[4]), who purifies the vanillin in the end through sublimation at 105°, is not perfect either, as according to H. J. Wichmann[5]) the aldehyde forms non-volatile decomposition products, when heated for some length of time to the above temperature. Wichmann heated pure vanillin for 3 to 6 hours at 105 to 108°, and obtained 4 to 5.6 per cent. of non-volatile, yellowish-brown residues, most likely oxidation and decomposition pro-

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[1]) *Swiss Patent* 89053 of April 16th, 1921. — [2]) *Swiss Patent* 91088 of October 17th, 1921. Supplement to 89053. — [3]) The alcoholic extract of vanilla is meant. — [4]) *U. S. Bur. Chem. Bull.* 152 (1912), 135; 162 (1913), 83. — [5]) *Journ. Ass. Offic. Agric. Chem.* 4 (1921), 479.

ducts of a complex nature. This indicates that the errors caused by the sublimation of the vanillin according to Hiltner's method, are considerable in the case of vanilla extracts containing more than 0.2 per cent. of vanillin.

Winton and his co-workers devised a lead number, now the official A. O. A. C. method, for analyzing vanilla extracts. In Wichmann's[1]) opinion it is not free from objection and he therefore publishes a new method of determining the lead number, supposed to simpler and more reliable.

To 175 cc. of boiled water in a liter flask Wichmann adds 25 cc. of 8 per cent. lead acetate solution and 50 cc. of vanilla extract, removes the alcohol by distillation, adds dilute sulphuric acid to the diluted and filtered residue and calculates the number of grams of metallic lead in the lead sulphate precipitated. This figure doubled is the required lead number.

Doherty[2]) says that the gravimetric determination of vanillin in vanilla essences can be avoided by a method based upon the reaction of the aldehyde with sodium bisulphite and the colour reaction with bromine water and ferrous sulphate. The author states that it is reliable and easily carried ont with the aid of Duboscq's colorimeter. A detailed description is given in the *Chemiker-Zeitung* 45 (1921), 687.

Thiercelin and Violet[3]) give the following information regarding the solubility of vanillin: Vaselin dissolves 11, glycerin 7 and oil 11 per cent. of vanillin at the ordinary temperature.

Solubility of Vanillin per litre.

	Water	Alcohol			
Temperature		15 per cent.	30 per cent.	60 per cent.	90 per cent.
10°	5,2 grams	50 grams	80 grams	755 grams	1 100 grams
20°	15,5 „	66,6 „	180 „	1 500 „	1 750 „
50°	44,4 „	166,6 „	750 „	3 000 „	5 000 „
78°	66,6 „	400 „	950 „	4 000 „	10 000 „

We found the following proportions[4]): —

Solubility of Vanillin in 100 parts by weight of the solvent at 10°.

Alcohol 96 per cent.	Alcohol 70 per cent.	Glycerin	Olive Oil	Liquid Paraffin
38 grams	30 grams	1 gram	0.9 gram	less than 0.1 gram

The vanilla crop in Madagascar, Comores and Réunion, amounting to 500 tons on an average, is estimated at only 350 tons for 1921. It is supposed that the United States consume 35, France 25, England 10, Switzerland 8, Scandinavia 8 and Germany, Holland and Spain together 14 per cent. of the crop[5]).

The following data are taken from an article on vanilla production in Mexico by Ch. H. Cunningham[6]): — At present Mexico employs over 50 000 people in the cultivation and extraction of vanilla. Vanilla (*Vanilla planifolia*, Andr.) is indigenous to the soil of Mexico[7]). It is principally cultivated in the districts of Papantla and Misantla in the State of Vera Cruz, the most productive region lying south-east of Tuxpan, between

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[1]) *Americ. Perfumer* **16** (1921), 301. — [2]) *Journ. and Proceed. Royal Soc. of New South Wales* **57**, p. 157. — [3]) *Parfum. moderne* **14** (1921), 153. — [4]) *Report* April **1909**, 144. — [5]) *Drug and Chemical Markets* **9** (1921), 405. — [6]) *Commerce Reports*, of November 20th, **1920**. As per *Americ. Journ. Pharm.* **93** (1921), 272. — [7]) Preuss considers the wild Mexican vanilla to differ from *Vanilla planifolia*. *Berichte d. Pharm. Ges.* **11** (1901), 24.

the rivers Nantla and Tuxpan. French colonists who settled on the banks of the Nantla river in the 19th century learnt the cultivation of vanilla from the natives and were soon successful. (According to Preuss[6]) the plantations were in a bad state in 1900 but have been enlarged continuously since.) The vanilla grows best in rich, sand soil, not drained too thoroughly, at an altitude of 1000 feet above sea-level. It is sheltered by the trees of the forest or by trees planted for that purpose.

There are different varieties of vanilla in the vicinity of Misantla. They are not so plentiful nor are they considered so good as the Papantla beans. These indigenous varieties are the *cimarror,* the *mestiza* and the *mansa.* When they are cured, only an expert can distinguish between the various classes. There is also a wild bean known as vanilla *platano,* which the Indians eat. This differs from the ordinary vanilla in that the plant is much smaller but has larger leaves.

In order to avoid plundering of their crops, the planters cut the vanilla early, sometimes in October and November instead of in January and February. As a result the beans weigh a pound less per thousand than they would normally.

For commercial purposes vanilla is divided into four classes: *grande fina* (20 cm.), *chica fina* (10 to 15 cm.), *zacata* and *basura.* The former two differ only in length, whereas their weight is almost the same. The *zacata,* which is a larger bean than the former two, grows more abundantly along the roadsides in the warm and hot regions of Mexico, where formerly it was considered to be without commercial value.

The exports from Mexico were as follows: in 1912/13 = 288766 kilos to the value of 3315471 Pesos; 1918 = 45066 kilos to the value of 505020 Pesos; 1919 = 197403 kilos to the value of 2333264 Pesos.

According to W. M. Doherty¹) Mexican vanilla beans average 2 per cent., Java and Bourbon beans about 2.75 to 2.9 per cent. of vanillin. Tahiti vanilla is but of little value in comparison, as it contains only 0.6 to 0.7 per cent. of vanillin.

Guadeloupe vanilla is generally classed among the inferior kinds²) although it may come very near the Mexican product if properly treated. As Ch. A. Smeltzer³) states the Guadeloupe planters have generally not cured the beans carefully enough nor in the proper way, so that their commercial value suffered. The Guadeloupe vanilla begins flowering in March, at which time the flowers are fecundated by the natives, who use a small wooden instrument (similar to a tooth-pick). Quite often the natives fecundate too many flowers on the same raceme with the result that the beans are apt to be thin and short. Another disadvantage is that the native planters gather the beans often immature (it takes about nine months for the vanilla to ripen). When thoroughly cured, this immature vanilla will result in a dry, ordinary quality bean; but the average curer, who is curing for weight and not for quality, permits the moisture to remain in the bean, with the result that his product reaches the market in apparently good condition, but soon gets mouldy. On the other hand, the fully-matured bean will never lose its good quality.

Frequently the beans are cured in Guadeloupe by the hot water method, which involves the smallest loss in weight. However, only the Mexican or sweating method, introduced in the island already 30 years ago by M. Fox, leads to a first class vanilla. Smeltzer has the beans assorted first and then "needled". This is done by making four scratches on the outer surface of the bean from end to end, deep enough to break through the skin, in order to permit the moisture to escape. This enables the bean to

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¹) *Journ. and Proceed. Royal Soc. of New South Wales* 57, p. 157. As per *Chem. Ztg.* 45 (1921), 696. — ²) Cf. *Reports* April 1902, 100; October 1909, 142. — ³) *Americ. Perfumer* 15 (1921), 197.

cure uniformly within as well as without. About 10 o'clock in the morning woolen blankets are spread on cement terraces, which by this time have become hot from the sunshine, each blanket being capable of holding about 25 kilos of green beans. Weather permitting, the various sized green beans are spread on the blankets and allowed to remain until 2 p. m. Then they are wrapped up in the blankets, folded tightly and turned upside down. After an hour's heating in this manner, the bundles are deposited in "sweating boxes" specially made to hold 500 kilos and not to permit any of the heat to escape. After 48 hours the boxes are opened and the vanilla is carefully gone over for mouldy beans. The others are again taken to the terraces, placed on other dry blankets and again given the sun. This heating and sweating process is repeated from eight to ten times, until the beans give off no more moisture and are sufficiently cured. The finished beans are dried on wire trays for two weeks, then assorted and packed into tins lined with wax paper.

Notes on Scientific Research in the Domain of the Terpenes and Essential oils.

General.

In a paper on the Oils, Fats and Waxes in Latin America, O. Wilson(1) gives a description of the principal essential oils manufactured in these countries. For the most part thuy are the products of the tropical regions of northern South America, Mexico, Central America, and the West Indies, the value of which products is but small compared with the resources. In Mexico, linaloe oil is distilled from the wood and also the seeds of various species of *Bursera,* in French Guiana the Cayenne linaloe oil from "bois de rose femelle", a strong-smelling wood said to derive from *Ocotea caudata,* Mez., a lauracea, and likewise the so-called Guiana sandalwood oil from wood originating apparently also from different lauraceæ(2). A similar oil, the so-called West Indian sandalwood oil, derived from the rutacea *Amyris balsamifera,* L.(3), has been shipped to Europe for over a century. It has been used as adulterant of, and substitute for, genuine sandalwood oil. The West Indies furnish furthermore orange oil (Jamaica), pressed and distilled oil of limes (Montserrat, Jamaica, Dominica), bay oil (Jamaica, St. Thomas, Guadeloupe, Antigua, Barbados, and Dominica), and pimento oil (Cuba, Haiti, Trinidad, San Domingo, Antigua, Leeward and Windward Islands, and Jamaica). The evergreen pimento tree, *Pimenta officinalis,* Lindl., also occurs in Mexico, Costa Rica, and Venezuela. Other possibilities of Jamaica, not yet developed, include vetiver and camphor. In Paraguay, the great number of bitter orange trees are made use of for the preparation of bitter orange oil and, to a limited extent, also of neroli oil. Another tree, the zygophyllacea *Bulnesia Sarmienti,* Lor., growing in Paraguay and Argentina, yields the important guniac wood oil, called erroneously also "champaca" oil(4).

Other essential oils and materials from which they can be distilled cover a wide range throughout the tropical forests of the Amazon and Orinoco Valleys and French Guiana. In Brazil, the leaves of a plant called "false jaborandi", *Arthante geniculata,* Miq. *(Piperaceæ),* yield a light-greenish oil of spicy mint-like odour and pungent burning taste; the leaves of *Citrosma oligandra,* Jul. *(Monimiaceæ),* called in Brazil *"catingueira",* furnish an oil with a greenish fluorescence and an odour resembling bergamot. The leaves of the wild lemon, *Citrosma cujabana,* Mart. *(Monimiaceæ),* contain an oil with an odour of bergamot and lemon, and those of the wild coffee tree, *Citrosma Apiosyce,* Mart., an oil with a lemon-like odour. From the bark of *Dicypellium caryophyllatum,* Nees, *"Cassia caryophyllata",* an oil is obtained containing eugenol and having a clove-like odour. In Bolivia, a grass grows abundantly which is closely related to lemon-

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(1) *Chem. and met. Eng.* 24 (1921), 1101. — *Bull. of the Pan-Amer. Union,* October 1921, 334, where the same article is published with two additional illustrations (evidently drawings) of the Paraguay petitgrain oil industry which are omitted in the *Chem. & met. Eng.* — (2) Cf. *Report* October 1911, 80. — (3) Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. III, p. 114. — (4) Genuine champaca oil has entirely different qualities and originates from *Michelia Champaca,* L.

grass and citronella grass and yields an oil similar to that of vetiver. In British Guiana and Brazil, the branches of the *pripriоca* tree *(Ocotea preciosa,* Nees, *Lauraceæ* — female *pripriоca*1)) contain an oil somewhat resembling linaloe oil. From Brazil, Venezuela and Colombia, copaiba balsam, from Salvador largely balsam of Peru, and from Colombia principally balsam of Tolu are exported. Mexico and Central America yield oil of turpentine. Finally, we mention vanilla and tonka beans which are grown in Mexico and the West Indies, and in Venezuela, Trinidad, Tobago, the Guianas, and Brazil respectively.

The National Committee on medicinal plants and plants yielding essential oil and extracts growing in Italy and the Italian colonies published a report2) on its activities in 1915 to 1919. The Committee was formed at the beginning of the war in order to propagate the cultivation and utilization of medicinal plants in Italy. The report enumerates the following plants, the cultivation of which come under consideration:— Peppermint, calamus, common and Roman chamomile, cherry laurel, lavender, balm (melissa), rosemary, thyme, valerian, anise, cumin, eucalyptus, fennel, rose, sage, and violets.— In the surroundings of Naples, and in general on the south coast, *inter alia,* various rose varieties such as *Rosa Hayi, R. Brünner, R. damascena, R. centifolia, R. Drusky* were cultivated. Since the cultivation would appear to pay — the oils extracted with ether were very fragrant —, it is intended to be continued. From fennel seed, melissa and laurel leaves, the blossoms of *Origanum vulgare,* L. and the leaves of *Lippia citriodora,* H. B. et K., the Institute of pharmaceutical Chemistry at the Naples University obtained, by distillation, a good yield of the essential oils.

A publication by W. W. Stockberger3) deals with the cultivation of drug plants in the United States. In numerous places in the Central and Eastern States the following drug plants have been found to thrive well:— anise, belladonna, caraway, chamomile, conium, coriander, digitalis, dill, elecampane, fennel, henbane, horehound, sage, stramonium, tansy, and thyme.— Aconite, arnica, lovage, poppy, senega, valerian, and wormwood seem to thrive best in the northern part of the U. S. where the rainfall is well distributed. On the other hand, cannabis, licorice, and wormseed are better suited to the warmer climate of the South. — Alethris, althaea, angelica, calamus, orris, pinkroot (*Spigelia marilandica,* L.), peppermint, serpentaria, and spearmint are adapted generally for situations where the soil is rich and moist, but lavender and larkspur prefer well-drained sandy soil. Ginseng and goldenseal (*Hydrastis canadensis,* L.) occur naturally on rich soil in the partial shade of forest trees. In addition to the plants mentioned, the following have further been cultivated:— cascara sagrada, castor-oil plant, *Pyrethrum cinerariaefolium,* Trev., *Lobelia inflata,* L., parsley, pokeweed, safflower, saffron, vetiver, wintergreen, and wormseed.

In a paper entitled, "Michigan, an important source of raw vegetable products", H. Kraemer4) reports on cultivation experiments started with about 50 drug plants in the botanical garden of the university of Michigan. As the experiments turned ont satisfactorily, Kraemer advocates a more extensive cultivation of the plants in Michigan. Of aromatic plants, spearmint and, above all, peppermint have been cultivated in that State. The peppermint oil industry, the development and history of which the author relates in full, started originally in Wayne County, New York, and was introduced into Michigan, Indiana, Ohio, and other states later. The climate and soil of Michigan

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1) Cf. *Report* April **1911**, 87. — 2) *Federazione pro Montibus, Pubblicazione* Nº 94, Rome, **1921**. — 3) *U. S. Dep. Agr., Farmer's Bull.* 663, August **1920**. — 4) *Mich. Acad. Sci. Report* No. 21, **1919**. As per a reprint kindly forwarded to us.

proved to be particularly favourable for the growing of peppermint, and the oil industry, therefore, developed here preferably well. The world's annual production of peppermint and spearmint oil amounts to about 600,000 lbs. Of this quantity, America — and principally Michigan — produces nearly one-half. Each acre yields about 30,000 lbs. of the green herb, which when distilled furnish to the utmost 100 lbs. of oil.

As to the origin of the peppermint industry, Kraemer's narrative runs as follows: — About 75 years ago there was a Yankee pedlar named Burnett who went through the country districts of Connecticut, Massachusetts, Vermont, and New York peddling tin-pans, rugs, chromos and other articles coveted by the farmer's families. The women had not a great deal of money, so Burnett hit upon a scheme of exchanging herbs in lieu of money for his merchandise. In the course of his travels he secured such quantities of peppermint so as to distil the oil by constructing numerous stills, especially in Wayne County, New York; he then gave up his peddling business and devoted himself to collecting and distilling the mint. Seeing the success of Burnett, a dealer H. G. Hotchkiss¹) became interested in the peppermint oil industry, sold the oil (not touched by American drug dealers) to Hamburg realising thereby a good profit, and soon started to work on an extensive scale. The farmers of Wayne County followed his example, and in a short time the industry spread throughout the county.

A preliminary statement of the general results of the 1919 census of manufactures, for the essential oil industry of the United States, has been issued by the Bureau of the Census, U. S. Department of Commerce²). In 1919, 77 establishments (1914: 103) produced essential oils (not included are synthetic and artificial oils) valuing $ 4411775 ($ 1289361). In Michigan, 29 establishments were located in Michigan, 22 in Indiana, 9 in Connecticut, 5 in New York, 4 in New Jersey, 3 in Pensylvania, 2 in Virginia, and 1 each in California, Kentucky, Ohio, and Tennessee.

According to the Census for 1920³), the total quantity of flavours produced in 1920 in the U. S. showed a reduction by 73 per cent. compared with the production in 1919, due principally to a greatly diminished output of saccharin and coumarin. New flavours reported in 1920 were benzyl acetate, benzyl cinnamate, cinnamyl propionate, ethyl cinnamate, methyl phthalate, and "vanilidine".

The production of perfume materials was 99470 lbs., valued at $ 332008 (138 per cent. gain compared with the value in 1919). The number of preparations increased from 24 to 41. The following were reported for the first time in 1920: — acetophenone, anisic aldehyde, cinnamic aldehyde, diphenylmethane, ethyl benzoate, ethyl phthalate, *iso*butylphenyl acetate, methyl benzoate, methylethyl acetate, methyl cinnamate, methylindole, phenylpropyl acetate, styrene, *iso*butyl salicylate, methyl guaiacol, benzylidene acetone, and *p*-cresol methyl ether.

We cull the following statements from a report⁴) of the Experimental Station for aromatic plants in Madagascar, located in Iroloina, near Tamatave, near the eastern coast of the island.

The cultivations in Nossi-Bé of the ylang-ylang tree started some years ago⁵) but given up later on have been started afresh in the last years although the blossoms are considered to be inferior to the Manila blossoms. Quite recently, the geranium, *Pelargonium roseum*, Willd. has been cultivated in Madagascar, hithertho with good

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¹) H. G. H. is to-day one of the oldest American trade marks, but it comprises only crude oil. — ²) *Drug and chem. Markets* 8 (1921), 1055. — ³) *Census of dyes and coal-tar chemicals* **1920**, 49. — ⁴) As per *Heil- und Gewürzpflanzen* 4 (1921), 126. — ⁵) Cf. *Report* October **1909**, 124.

success. From the Moramanga and Fianarantson districts, large quantities of geranium leaves are exported. In the island of Mayotte belonging to the Comoro Islands, in the north-west of Madagascar, the cultivation of mint, sage, verbena[1], and especially patchouli has been started.

The clove tree, *Caryophyllus aromaticus*, L., is very common in Madagascar, particularly in the rainy district of Ste.-Marie, Movrantsatra, and Tamatave. In 1918, 200 tons of cloves were exported from Ste.-Marie.

The principal export commodity of Madagascar is the vanilla bean, which is cultivated in the north-western coast and the volcanic districts of the island, in Nossi-Bé, and the Comoro Islands. In Antalaka, on the northern coast of Madagascar, the annual turnover of vanilla amounts to 100 tons. In order to drain the fever districts and to protect other cultivations, the eucalyptus tree, *E. Globulus*, Lab. has been successfully grown in many parts of Madagascar. Likewise, nutmeg trees (*Myristica fragrans*, Houtt.) are cultivated in several places of that island.

Of wild-growing aromatic plants of Madagascar, the following may be mentioned: — the hazamalanga tree, the fruit of which is said to contain an oil with a strong aromatic oil[2]; *Ravensara aromatica*, Gærtn., a lauracea with aromatic leaves and bark; *Angrœcum fragrans*, Thou., an orchidea, the leaves of which, smelling of coumarin, are used for scenting tea; finally, a *Canarium* species with a fragrant resin.

According to an article in *The Chemist and Druggist of Australasia*[3], the large plant installed by G. J. Adcock in New South Wales for the preparation of the essential oils of orange, lemon, lavender, geranium, and peppermint appears to meed with good success. Wages in Australia are low compared with those in other countries, and a further advantage is the encouragement given by the Excise regulations which permit the use of duty-free Australian spirit provided it is converted into the primary perfume by adding other Australian products so as to effectively denaturise the spirit.

Some thirty-five years ago the Victorian Government established a "perfume farm" which was at first remarkably successful, but owing to lack of interest on behalf of the new Goverment, turned out a failure after some time. A sad mistake, too, was that the French methods for obtaining oils had been copied, *e. g.* the "enfleurage à froid" process, withouth due regard to their suitability for Australian products, and even without exact knowledge how these processes were to be carried out properly.

According to a note in the *Chemiker-Zeitung*[4], the Spanish distillers of essential oils refrain from distilling large quantities of oils, more especially of thyme oil, owing to their unfavourable financial situation, and the slow demand of Spanish oils ruling since October 1920. The principal buyers of thyme oil are the Americans who prefer the oil of *Tomillo carasqueno*, a *Corydothymus* species growing in Southern Spain and rich in carvacrol, while the French patronise the oil from *Tomillo rojo* (*Thymus vulgaris*, L.) with but 20 to 47 per cent. of phenols, of which 30 to 35 per cent. thymol.

A question in this respect was kindly answered by Mr. Felix Gutkind[5], Malaga, as follows: — The statements in the *Chemiker-Zeitung* are perfectly correct. Only very little rosemary oil has been distilled; but this oil can be distilled at any time of the year, except in the months with excessive rainfall, so that the stocks, when scarce,

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[1] From the abstract available it is not clear whether it is the case of the true verbena, *Lippia citriodora*, H. B. *et* K., or of the so-called Spanish verbena, *Thymus hyemalis*, Lange. — [2] From hazamalanga *wood*, Bois de Cass, originating from *Hernandia peltata*, Meissn. of Madagascar we obtained years ago 1.03 to 2.06 per cent. oil with an odour of perilla aldehyde. The oil obtained from the *fruits* (0.5 per cent.) did not show this odour. — [3] *Chemist and Druggist* **95** (1921), 48. — [4] *Chem.-Ztg.* **45** (1921), 776. — [5] Letter of Aug. 31, 1921.

can be renewed within a short time. The only question is whether the cutters are willing to suffer a reduction of their wages as long as the victuals remain so dear in Spain. In many cases, rosemary oil has been sold to foreign countries with loss or at least without profit merely with the object to secure means for distilling thyme oil, the yield of which was likewise very low as compared with former years.

France and equally England, it is true, have purchased a good quantity of oil rich in thymol, since both countries make use of thymene (? a mistake in lieu of thymol). The U. S. are and were buyers of *Corydothymus* oil sampled to you recently. Much of this oil is also shipped to Grasse. In the preceding years, the bulk of the oil from *Thymus vulgaris* in Spain has been worked up for thymol production.

As to the result of the yield of spike oil, nothing definite can be said as yet. High-priced stocks from 1920 still exist. The 1921 crop will most certainly be but one-fourth of the 1920 one, and the 1921 production is most probably to be limited by the owners of old stocks with the view to justify the high price of the old crop as soon as a lively demand appears.

As per a report of the Administration of Mysore[1] for the year ending June 30, 1920, a number of satisfactory essential oils are distilled there. Important results were obtained in the distillation of cardamoms. Nearly two tons of patchouli leaves were distilled, and the oil was used for perfumery purposes. Qualitative experiments were done in the distillation of rosha grass, vetiver, lemongrass, citronella grass, *Kasturi arsina*[2], and ajowan seeds.

J. A. Hugues[3] gives a description of an apparatus serving for *extracting the odorous principle* with volatile solvents from plants, roots, leaves, flowers, even from gums (!) and resins. Two endless movable chains circulate within the extraction pan and carry a series of boxes which travel continuously from top to bottom and *vice versa,* as in a dredging machine. The extractor contains a sufficient quantity of liquid, such as light petroleum, carbon disulphide, or ethyl chloride, so that the lowest box at a time is completely submersed in the solvent. The bottom, lid, and the side walls of each box are perforated. The boxes are then filled with the drugs for extraction and worked continually through the solvent until the latter is saturated with the perfume. The major part of the solvent is then drawn off by means of a pipe at the bottom of the still, and by distillation the liquid is separated into solvent and odorous residue. The solvent retained by the drug may recovered by steam-distillation of the boxes. Owing to the low loss of solvent this process seems to be preferred to other methods[4].

A. Koehler[5] has constructed a contrivance for abstracting automatically the odorous principle from flowers. The flowers are fed from a hopper on a circulating greased belt running over two cylinders. After a certain time the flowers are stripped off from the belt.

The recovery of essential oils from the distillation waters by cohobation is stated, in a communication by J. de Lorgues[6], to have been introduced in Southern France about ten years ago by Charabot and Laloue. We beg to point out that in the Barrême factory, erected by Schimmel & Co. in 1905, this well-known process has been made us of in the distillation of lavender oil.

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[1] *Americ. Perfum.* **16** (1921), 107. — [2] We were hitherto unable to ascertain what is meant by *Kasturi arsina.* Probably, it is the case of *Kasturi arishina = Curcuma aromatica,* Salisb., or *Kasturi bhendi = Hibiscus Abelmoschus,* L. (Cf. Dymock, Warden, and Hooper, *Pharmacographia Indica,* **1890.**) — [3] French Pat. 505085, Oct. 1, **1920.** — [4] Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. I, p. 247. — [5] French Pat. 518713, May 30, **1921.** As per *Chem. Zentralbl.* **1921,** IV. 596. — [6] *Perfum. Record* **12** (1921), 143; *Chemist and Druggist* **94** (1921), 855.

In the same article, a second process, devised by Gattefossé, is described for recovering essential oils from the distillation waters. The aqueous distillate passes in a very fine spray a layer of rectified petroleum in a closed vessel about one-third full. The water is fed from above, gives off its oil content to the hydrocarbon, separates at the bottom of the vessel and is siphoned off. This washing process is repeated several times. The oil obtained after evaporating the solvent is not nearly of the same quality as the oil resulting from direct distillation.

Another process for recovering the essential oils suspected in the distillation waters has been patented by J. Amic, L. Roure, J. Roure, and P. Magiapan[1]). The water being separated from the oil in a receiver is conducted to the upper part of a distillation-column filled with coke pieces where it meets the vapours ascending from the still. The condensed liquid is siphoned off, while the vapours leaving the column are cooled in a condenser and then conducted to the receiver for separation.

As to the "water oils" of various plants, we refer to pp. 48, 50, 58 and 59 of this *Report*.

Essential oils showing a tendency to *resinify* and to acquire a turpentiny odour are said to keep for an infinite time after adding for each 500 gr. of oil 3 gr. of sodium hydrogen sulphite[2]).

In France, a patent has been granted to Lautier Fils[3]) for a process of manufacturing *pomades* whereby the "châssis" an prepared mechanically for the enfleurage process, *i. e.*, coated with fat and fed with flowers. The latter drop automatically from a hopper on the greased "châssis" which pass the hopper on an endless belt.

H. Schelenz[4]) furnished a small contribution towards the *history of odoriferous and toilet preparations.* Mankind has made use of these articles, more especially of the odorous drugs, from the very beginning. The Bible already mentions these preparations, without, however, giving credit in this respect to the achievements of the ancient Indians, Persians, and Egyptians. In the course of time, one got acquainted with the methods for obtaining the pure odoriferous substances and how to modify the original ways of using them. The scented powders, bags, pomades and sticks were substituted by products of distillation, either the essential oils proper, or to their alcoholic solutions. In the 13th century, for instance, we hear of a "Hungarian Water" rosemary water) which was distilled from the strong-smelling rosemary at first with water, later on with wine. The dispensaries of the Italian, later on also of the French and German monasteries, where the volatile oils were distilled already in the Middle Ages, acquired in the course of time a high standing. In the 18th century, the Carmelites traded an *"Eau des Carmes"* essentially an aqueous distillate of balm (melissa) used for medicinal purposes, and some time after, the Italians made known in Cologne the *Acqua della Regina*, or *"Eau de Cologne"*. This preparation is, in Schelenz' opinion, the earliest specimen of an alcoholic solution of essential oils.

Bibliography.

In Ullmann's *"Enzyklopädie der technischen Chemie"*, vol. IX (1921), the odoriferous bodies (*"Riechstoffe")*, are fully dealt with. The compilers, A. Hesse, A. Ellmer, and R. Haarmann, after giving a short historical introduction (starting from the fundamental

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[1]) French. Pat. 521 713, July 3, 1920. As per *Chem. Zentralbl.* 1921, IV. 1016. — [2]) *The Spatula* 26, 10. As per *Pharm. Zentralh.* 62 (1921), 462. — [3]) French Pat. 524595, Sept. 7, 1921. — [4]) *Seifensieder-Ztg.* 48 (1921), 797.

work of Tiemann and of Wallach and furnishing a review of the recent development of the technology of the aromatics), deal with the process for preparing odoriferous substances and give furthermore a description of the complex aromatics, their constituents, and how the simple and the complex aromatics are obtained artificially. In the chapter *"Allgemeine Methoden zur Gewinnung der Riechstoffe"* (General methods for preparing odoriferous substances), Hesse enters with particular interest into the distillation of otto of rose in Bulgaria, with which process he is acquainted owing to personal inspection. He describes, *inter alia,* a duplex still for distilling roses (illustration) furnished by Egrot, of Paris, which shows some handsome and practical details, just like the most of French machinery, but on the other hand, exhibits several serious drawbacks. Various contrivances, *e. g.*, the badly-constructed still-head, show clearly that the French, unlike the German manufacturers, have not taken the trouble to study from a scientific standpoint the process of the steam-distillation or the water-distillation of plants. — In the chapter dealing with the natural complex odoriferous bodies, the more important essential oils, a well as various aromatics of vegetable or animal origin, their hitherto known components, and the analytical methods serving for the examination of these products are enumerated. — The components of essential oils, insofar as the occur as separate trade articles in the industry of aromatics, have been treated in detail by the authors. For instance, the numerous processes for obtaining vanillin, either from the natural products, or by synthesis, are fully dealt with. — In the last chapter, *"Künstliche Darstellung einfacher und komplexer Riechstoffe"* (Artificial preparation of simple and composed aromatics), the authors demonstrate, by various instances, how nearly all the ingredients of natural perfumes can be obtained by chemical means. In addition, many works processes for synthesising these products are communicated. A short compilation of statistical figures illustrating the German import and export of essential oils and aromatics during the last decades and showing the rapid evolution of the German *"Riechstoff"* industry prior to the War, forms the last chapter of this treatise which is equally will furnished with illustrations and literary notes.

Towards the end of the 19th and the beginning of the 20th century, the cultivation of medicinal plants in Germany, as well as in other European countries, such as Holland, had gone down seriously. Since the beginning of the Great War, however more especially in the last years, a change has taken place, to which we referred repeatedly[1]). It was a necessity and an act of material self-respect to cover the demand for medicinal plants from home-grown products. People started again, more especially in Central and Southern Germany, to collect and cultivate drugs on a larger scale. These endeavours were aided by numerous societies, *e.g.*, the "Committee for propagating the collection and cultivation of medicinal and economical plants by Government measures" *(Ausschuß zur staatlichen Förderung der Sammlung und des Anbaus arzneilich, wirtschaftlich und technisch verwertbarer Pflanzen)* at Dresden, the "Hortus-Society" and the "Society for the promotion of the cultivation and collection of medicinal and aromatic plants" *(Gesellschaft zur Förderung des Sammelns und des Anbaus von Gewürzpflanzen)* in Bavaria, and by the German Pharmaceutical Association *(Deutsche Pharmazeutische Gesellschaft)* of Berlin. However, these endeavours and suffered opposition from various quarters. One of the objections made seemed to be somewhat justified insofar that it was considered unwise to enlarge the area used for drug cultivation in stead of cultivation of victuals and fodder, or of important vegetable raw-materials

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[1]) Cf. *Reports* 1917, 110; 1918, 78.

for industrial purposes. The question arose, is it commendable from an economic standpoint or not to increase the cultivation of medicinal plants in Germany.

Th. Sabalitschka[1]), in an investigation entering very closely into this question, comes to the certain conclusion that in Germany the cultivation of medicinal herbs is in any case a serious necessity which, provided the proper herbs are selected, is particularly provitable for small growers. After dealing with the cultivation of drugs in Antiquity and the Middle Ages, Sabalitschka enters upon the following points:— *a.* consumption in Germany, prior to the War and in future, of drugs obtainable in the country itself; *b.* drug imports into Germany prior to the War; *c.* profitableness (from the producer's view) of drug cultivation; *d.* advantages of cultivating drugs for Germany's trade in general; *e.* directions how to cultivate succesfully medicinal and aromatic herbs in Germany; *f.* cultivation of drugs in states other than Germany, and acknowledgement of the necessity of promoting the cultivation.

Since Sabalitschka's paper touches but lightly our own domain, we content ourselves with the above review. In any case, we recommend sincerely the perusal of this extensive paper which is well supplemented with statistical data on drug imports and exports.

In addition to several short bulletins (in the manner of the Circulars of the Departement of Agriculture, U. S. A.), the Italian "Federazione pro Montibus" has published[2]) a *dictionary* giving the vernacular names of the Italian medicinal and aromatic plants and the corresponding Latin terms.

K. Bournot[3]) gives a *review* for 1920 of the research work on terpenes and essential oils.

Analytical Notes.

K. Hoepner[4]) deals with the various methods *for estimating the alcohol content* in presence of volatile substances. He discusses six methods worked out by the German Alcohol Monopoly Office for determining the free alcohol, not combined with acids, in mixtures of spirit with neutral volatile bodies (perfumes, hair tonics, mouth washs, mixtures of alcohol and esters, with exception of methyl alcohol and of so-called fusel oil) and compares the results with his own experiments. Two of these methods, *a*) diluting and salting out the sample, then distilling and taking the specific gravity of the distillate, *b*) chromic acid process without previous skaking out with sodium sulphate and light petroleum, proved to be unreliable and should be abandoned. Equally the method consisting of diluting with salt solution, then shaking out with light petroleum and distilling the spirit, cannot be recommended. Of the remaining three processes the one consisting of calculating the alcohol content direct from the specific gravity is appliable only in cases when the composition of the preparation is known as to the density and quantity of the dilute alcohol and of the dilute volatile constituent; in addition, a table for calculating the actual alcohol strength must be consulted. The method basing on the process of diluting and shaking out with light petroleum of the neutral volatile ingredients, where the alcohol present is calculated from the density of the distillate, furnishes values which are in the most cases too

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[1]) *Über die Notwendigkeit des Arzneipflanzenanbaus in Deutschland, über seine Rentabilität und seine Vorteile für die deutsche Volkswirtschaft und über die zweckmäßigste Inangriffnahme der Medizinalpflanzenkultur in Deutschland.* Berlin, published by Gebr. Bornträger, **1921**. As per a copy kindly forwarded to us. — [2]) Domenico Saccardo, *Dizionario dei nomi vulgari delle piante medicinali e da essenze più in uso e dei corrispondenti scientifici latini. Arch. di Farmacognosia e Scienze affini,* vol. 8, **1917**. — [3]) *Chem. Ztg.* **45** (1921), 531. — [4]) *Zeitschr. Unters. d. Nahrungs- u. Genußmittel* **41** (1921), 193.

low, anyhow the errors can be eliminated to some extent by certain manipulations. The frequent emulsions occurring here are a great drawback. Satisfactory results are obtained by the following chromic acid process: — dilute with sodium sulphate solution, extract with light petroleum, oxidise the alcohol with potassium bichromate and sulphuric acid to acetic acid, calculate the alcohol present from the amount of bichromate consumed — but only if the portions of water-soluble esters remaining in the sulphate solution are duly taken in consideration, as well as the increase in volume caused by solution of the volatile components. For carrying out this bichromate process, small quantities, say 5 ccm., are sufficient.

The author finally gives the following improved directions for estimating the alcohol contained in alcoholic preparations together with volatile substances *a*) by means of the specific gravity, *b*) by the chromic acid process: —

a) 50 gr. of the sample, which must be free from glycerin, resins, or other extract substances, are given into a separating funnel, 50 gr. water then added, finally 50 cc. light petroleum ("petroleum benzine") and shaken vigorously several times. The next day, the lower layer is given into a tared flask and brought to 99 gr. The alcohol content as calculated from the density must be multiplied by 2. Special directions are given for removing glycerin, resin, or free acids before carrying ont the estimation, in case these bodies should be present.

b) 25 or 50 cc. of the sample (according to the preliminary alcohol content as calculated from the density) are given into a tared flask containing about 25 cc. of water, then weighed and diluted up to 500 cc. with a 12.5 per cent. solution of sodium sulphate. The mixture is shaken repeatedly and vigorously with petroleum benzine, the sulphate solution drawn off when fully clear and shaken with fresh 50 cc. petroleum benzine. The next day 10 cc. of the fully clear sulphate solution are mixed with 25 ccm. 2N-potassium bichromate solution and 50 cc. dilute sulphuric acid and cooled down under the tap. After a lapse of two or three hours, the mixture is transferred into a 500 cc. measuring flask and water is added up to the mark. Of this solution, 50 cc. are mixed with 20 cc. potassium iodide solution, then diluted, after 10 to 15 minutes with about 100 cc. water and titrated balk with decinormal sodium hyposulphite solution, using starch solution as indicator. — In order to ascertain whether the sodium sulphate solution used for the oxidation still contains a small amount of water-soluble esters, 200 cc. of the sulphate solution are mixed with 10 cc. standard alkali solution, and the next day the amount of alkali not required for saponifying the esters possibly present is titrated back with standard acid. An amount of 0.2 cc. alkali is not considered. — Each cc. decinormal bichromate or hyposulphite solution = 0.0011512 gr. alcohol. — Glycerin, resins, free acids or bases are removed before carrying out the examination, as stated above.

W. Olczewski[1]) gives the following directions for estimating the alcohol content in essences: — 25 gr. of the liquid under examination, 25 gr. saturated salt solution, and 20 gr. petroleum ether (b. p. not exceeding 60°) are given into a separating funnel, shaken thoroughly and as soon as the liquid is clear the lower layer is drawn off into a 300 cc. flask. The residual petroleum ether is shaken once more with 15 cc. salt solution, the aqueous layer is given into the flask and the contents, after adding some magnesium carbonate and débris of porous plate, are distilled into a pyknometer of 50 cc. capacity.

When liquids show a strong tendency to emulsify with petroleum ether, or are rich in essential oil, double distillation is resorted to. From 25 gr. of the preparation and 50 gr. water, with addition of some alkali about 50 cc. are distilled (in case of foaming, the alkali is omitted, and tannin is added) directly into a separating funnel, the distillate is saturated with salt, then shaken out with 25 cc. petroleum ether, drawn off into a 300 cc. flask (the petroleum ether is likewise shaken out once again with salt solution), and the united aqueous liquids are again distilled, as in the first-mentioned process, into a pyknometer of 50 cc. capacity.

The methods published hitherto for the detection of alcohol in essential oils are discussed by Utz[2]). We abstain from mentioning them here, since the author likewise has found them to be more or less unreliable. The process described in Gildemeister's

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[1]) *Pharm. Zentralh.* 62 (1921), 288. — [2]) *Deutsche Parf. Ztg.* 7 (1921), 217.

text-book1) serves best for qualitative tests (formation of iodoform) and for approximate quantitative determinations (shaking out a fairly large portion with water or salt solution).

The process devised by Verley and Boelsing2) for the quantitative *estimation of alcohols and phenols* (more especially of santalol, menthol, and eugenol) has been re-examined by H. W. van Urk3). The result was this that none of the substances mentioned above can be estimated accurately by that method. Since years ago we entered fully into the details of the process and found it to be unreliable4) we consider it unnecessary to occupy ourselves furthermore with van Urk's publication.

In order to *determine the amount of phenols* in essential oils the method devised first by Gildemeister5) for testing thyme oil and improved later on by us6) has, in general, proved satisfactory; it consists in shaking 10 cc. oil in a cassia flask of fully 100 cc. capacity with a caustic soda solution of 3 or 5 per cent., and calculating the phenol content from the amount of the oil dissolved in the lye. W. H. Simmons7) proved by way of experiment, that with thyme and cinnamon leaf oils 5 cc. oil on treatment with a 5 per cent. caustic potash lye, give a distinctly higher proportion of phenols than when 10 cc. of the oils are employed. Hitherto, the author was unable to prove with certainty whether the lower or the higher values were the correct ones. Comparative tests with clove, bay, and pimento oils gave the same results with 5 or 10 cc. oil. (On the whole, too strong lyes give too high results, since the lye, in connection with the phenol alkali, dissolves also part of the non-phenols. For this reason, we shake some oils, *e. g.*, clove oil, with a caustic solution of but 3 per cent.)

With the object to determine the composition of mixtures of eugenol and *iso*eugenol, in the preparation of vanillin from eugenol, P. V. McKie8) constructed a curve illustrating the melting points of mixtures of pure eugenol and pure *iso*eugenol benzoates, m. p. 69.5 and 104° respectively, following the method described in a previous paper9). A well-marked eutectic point was observed at a temperature of 56.5°, corresponding with a composition of 25.5 per cent. of *iso*eugenol benzoate. Although at temperatures from 83 to 86°, and at compositions approximating to the equimolar mixture, the curve showed a discontinuity, the use of the melting point as a means of determining the composition of mixtures is thereby not invalidated.

The authoress obtained the esters by dissolving the crude oil, resulting from the isomerisation of eugenol, in pyridine, and treating with some 25 per cent. excess of benzoyl chloride. The major portion of the benzoates separates as a solid, and a further quantity on pouring the pyridine solution into dilute sulphuric acid. The resulting benzoates were dissolved in ether, from which, on evaporation of the ether, the solid benzoate mixture is obtained.

When, years ago10), we *estimated citronellol* according to the formylation method, we found that part of the alcohol undergoes a change. In order to elucidate this reaction, A. St. Pfau11) formylated each 100 gr. of citronellol (b. p. 105° [7.5 mm.], 6 months' old preparation) by boiling for one hour with each 200 cc. of 100 per cent. and of 85 per cent. formic acid. The formylation products (ester v. 295.4 = 96.4 per cent.,

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1) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 612. — 2) Cf. *Report* April **1902**, 25. — 3) *Pharm. Weekblad* 58 (1921), 1265. As per *Chem. Zentralbl.* **1921**, IV. 1145. — 4) Cf. *Report* April **1903**, 27. — 5) Hager, Fischer and Hartwich, *Kommentar zum Arzneibuch f. d. Deutsche Reich, 3. Ausg.* Berlin **1892**, 1st ed., vol. I, p. 377. — 6) *Report* April **1907**, 119. — 7) *Perfum. Record* **12** (1921), 394. — 8) *Journ. chem. Soc.* **119** (1921), 777. — 9) *Ibid.* **111** (1918), 799. — 10) Cf. *Report* October **1913**, 64. — 11) *Journ. f. prakt. Chem. N. F.* **102** (1921), 276.

and 263.0 = 84.3 per cent. citronellol) were separated into 6 and 5 fractions respectively. It was then found that there had been formed on the average, in formylation:—

	With the 100 per cent. acid	With the 85 per cent. acid
Terpenes and citronellol.	1 per cent.	3 per cent.
Citronellyl formiate	20 „ „	30 „ „
Citronellyl glycol monoformiate[1]	35 „ „	40 „ „
Citronellyl glycol diformiate[2] .	29 „ „	12 „ „
Residue, polymerized	15 „ „	15 „ „

By the same treatment, citronellyl formiate gave rise to a product of the following composition:—Unchanged citronellyl formiate, 35 per cent.; citronellyl glycol diformiate, 50 per cent.; polymerized residue, 15 per cent.

Hence the exceedingly high values obtained by determining pure citronellol by the formylation method[3]), are due to the formation of citronellyl glycol diformiate.

Pfau concludes, as result of his work, that the formylation process for estimating citronellol furnishes irregular values and affords no clue as to the true content of citronellol. This is nothing novel, as we always have pointed out[4]) that this process is not an exact one, although it may be satisfactory in practical work.

Equally, C. T. Bennett[5]) tested the formylation method by varying the conditions and came to the conclusion that the method is unreliable for the determination either of citronellol or citronellal.

With regard to these two articles by Pfau and Bennett, W. H. Simmons[6]) is of opinion that both workers confirm his own conclusions on the subject, but apparently ignore what he considered to be most important, *viz.*, that the method is a very useful one for comparing the relative proportions of citronellol in different geranium oils, as was suggested by him in 1913. Subsequent experience with a very large number of samples of African and Bourbon geranium oils fully confirmed the view which Simmons then expressed. It is very important to adhere strictly to one and the same direction and to heat for exactly 60 minutes on a boiling water bath, and not on a sand bath.

For the *estimation of terpin hydrate* in elixir of terpin hydrate Nat. Form.[7]), A. G. Murray[8]) gives the following directions:—The elixir is mixed with a solution of 20 gr. common salt in 100 ccm. of water until the alcohol content is from 10 to 15 per cent. by volume. The mixture is shaken out with four portions, one-fourth volume each, of chloroform containing 5 to 7 per cent. by volume alcohol. Each portion of the solvent is washed successively with 5 ccm. salt solution, then filtered into a tared beaker, and evaporated by aid of a blast, avoiding application of heat. (On evaporating an alcoholic solution of terpin on the water bath, about 10 per cent. of the terpin hydrate were found to volatilize.) The residual pure terpin hydrate is dried at the open air and then weighed. The error was only +0.8 per cent.

The acetylation of both hydroxyl groups in terpin may be carried out by boiling the glycol for three hours with eight times its weight of acetic acid and five times its weight

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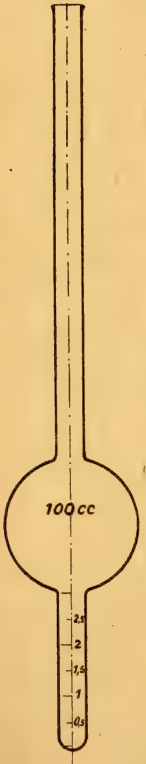
[1]) d_{15° 0.9651; $\alpha_D + 1^\circ 46'$; n_{D15° 1.4488. — [2]) d_{15° 0.9976; $\alpha_D + 1^\circ 33'$; n_{D15° 1.4425. — [3]) Cf. *Report* October **1913**, 64. — [4]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 600. — [5]) *Perfum. Record* **12** (1921), 351. — [6]) *Ibidem* 398. — [7]) It contains, in addition to about 1 grain (0.175 gr.) of terpin hydrate, tincture of sweet orange peel, spirit of bitter almond, alcohol, glycerin, and syrup in 1 fl. dr. — [8]) *Journ. Amer. pharm. Ass.* **10** (1921), 440.

of a neutral solvent, *e. g.*, turpentine oil, with addition of sodium acetate. Basing on this reaction O. Fernandez and N. Luengo[1]) worked out a method for the estimation of terpin.

Although the inaccuracy of the phosphoric acid process for the *determination of cineole* is long known — even C. E. Sage and J. D. Kettle[2]) admit readily that the method is not so exact as a purely chemical method — we very frequently meet with endeavours to puff up that process whenever an opportunity arises. Such an opportunity arose recently with the publication of Tusting Cocking's cresineol method[3]) and Kleber's and von Rechenberg's[4]) solidification point test. Sage and Kettle point out that the former author[5]), when comparing the "phosphoric" and "resorcinol" methods, found considerable discrepancy between the results of both methods (which fact we take as proof for the inaccuracy of the "phosphoric" method), and now they publish the results of comparative cineole determinations in a few eucalyptus oils and cineole samples, carried out according to the "phosphoric", cresineol, and solidification point methods. The results which differ to the utmost by 6 per cent. and are hardly worth any discussion, are, in our opinion, not in favour of the phosphoric acid process, as the authors maintain.



F. B. Power[6]) recommends the following process for *detecting methyl anthranilate* in fruit juices:—From 500 ccm. of the liquid 200 ccm. are distilled off, and the distillate which in presence of an appreciable quantity of the ester shows a bluish fluorescence, is shaken out three times with each 10 ccm. of chloroform (*not* ether). The residue obtained on careful evaporation of the chloroform extract is immediately treated with 2 ccm. of 10 per cent. sulphuric acid, the acid liquor is transferred to a test-tube and cooled. To the liquor one drop of a 5 per cent. solution of sodium nitrite is added, then a few crystals of urea, and subsequently one of the following two reagents:—*a.* a mixture of one ccm. of a 0.5 per cent. solution of pure β-naphthol containing 0.2 per cent. of sodium hydroxide, one ccm. of a 10 per cent. solution of sodium hydroxide, and one ccm. of a 10 per cent. solution of monohydrated sodium carbonate, $Na_2CO_3 \cdot H_2O$. If not less than 0.0001 gr. of methyl anthranilate is present, a yellowish-red precipitate will be produced; *b.* one drop of dimethylaniline, and, when the latter has completely dissolved, a slight excess of a 10 per cent. solution of sodium hydroxide. The yellowish coloration produced in presence of not less than 0.001 gr. of the ester changes to red on slightly acidifying the mixture with dilute sulphuric acid.

By this process the author believes to have overcome the errors such as possible with the Erdmann method[7]) (incomplete separation of the ester which is not free from foreign admixtures). The results of the investigation of grape juices by this process are reserved for a future communication.

The *estimation of phenylacetaldehyde* in the cassia flask according to the bisulphite method is often connected with difficulties and is frequently inexact, since the heavy non-aldehydic (polymerized) constituents of the aldehyde remain at the bottom of the flask. A. Reclaire[8]) recommends to modify the process as follows:—

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[1]) *Ann. soc. española Fis. Quim.* [2] 18 (1920), 158. As per *Chem. Zentralbl.* **1921**, IV. 687. — [2]) *Perfum. Record* **12** (1921), 44. — [3]) Cf. *Bericht* (German) **1921**, 65. — [4]) *Ibidem* 35. — [5]) Cf. *Report* October **1910**, 67. — [6]) *Journ. Amer. chem. Soc.* **43** (1921), 377. — [7]) *Berl. Ber.* **35** (1902), 24 and 2355. — [8]) *Perfum. Record* **12** (1921), 341.

5 ccm. of phenylacetaldehyde are introduced into a 100 ccm. flask of special construction, then 20 to 25 ccm. of solution of sodium bisulphite (containing about 30 per cent. $NaHSO_3$); the mixture is shaken vigorously for some minutes, and the whole is placed in a water-bath. After some time, boiling water is gradually added until the solid compound at first produced is completely dissolved. More water is then added, and the non-aldehydes settle down in the graduated tube, where the volume can be read off when cold.

As to the *identification of nitrobenzene* when present in bitter almond oil, see p. 6 of this *Report.*

Re the *estimation of vanillin* according to Doherty see p. 100 of this *Report.*

Physical Notes.

As is generally known, the reason why the vapour tension curves of two substances do not run parallel to each other is to be found in the difference of the changes of tension with identical changes of the temperature. The numerous curves compiled by C. von Rechenberg¹) show that about 2000 pairs of curves cross each other. When, in agreement with v. Rechenberg, the liquid and solid states are considered as chemical formations which on heating are decomposed into vapour molecules, then the different stability of the molecular complexes is the cause of the varying evolution of vapour, hence the latter is a measure for the former. When working out the entire material v. Rechenberg was able to classify all the substances investigated in relation to the increase in vapour pressure for the equal rise in temperature, and this classification was clearly in accord with Rothmund's²) solubility series. It may, therefore, be concluded that in both cases the regularity is a result of the identical cause mentioned above.

Furthermore, C. von Rechenberg³) utilized his excellent material of vapour tension curves for testing Bancroft's rule which implies that all mutually soluble liquids of which the vapour tension curves cross each other form "distinguished" mixtures with either a minimum or maximum boiling point. v. Rechenberg was able to confirm the general applicability of that rule, but with the restriction that such mixtures with "distinguished" boiling points are limited to a certain range of pressure.

With the object to investigate in the laboratory the separation of binary mixtures by continuous distillation, A. F. Dufton⁴) constructed a continuous still with a still-head as had been devised by S. F. Dufton⁵). The mixture to be separated was fed from a small flask, where it was electrically pre-heated to its boiling point, into the middle of the column. A siphon kept the level in the preheater constant. The lower part of the still was also heated electrically by a wire coil and the current required was measured by a watt-meter. To obviate any loss of heat from the lower part of the column, a thick lagging of cotton-wool surrounded by a steam-jacket was employed. Exact thermometers at the top of the still-head and at the bottom of the column indicated the purity of the separating products.

Starting from a 50 per cent. mixture of benzene and toluene the author succeeded in regulating the still to work automatically, yielding pure benzene and pure toluene continuously. By measuring the head supply it was found that the separation of one

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¹) *Zeitschr. f. physik. Chem.* **99** (1921), 87. — ²) *Ibidem* **26** (1898), 489. — ³) *Ibidem* **99** (1921), 105. — ⁴) *Journ. chem. Soc.* **119** (1921), 1988. — ⁵) *Journ. Soc. chem. Industry* **38** (1919), 38 T; *Bericht* (German) **1920**, 101.

gram of benzene required 1340 calories. As the theoretical quantity of heat required is calculated to be 208 calories[1]) the thermal efficiency of the still was 15.5 per cent.

When other still-heads were employed, for instance copper gauze discs, or thin-walled cylindrical glass beads 4 mm. long and 4 mm. in diameter, the thermal efficiency[2]), with a 50 per cent. mixture of both hydrocarbons, was up to 47 per cent.

L. Smith[3]) publishes some laboratory notes on the efficiency of still-heads in vacuum distillation. We agree with the author that the circumstances, in vacuum distillation, are not fully comparable to those under atmospheric pressure; in the present case, however, the method employed for testing was not sufficiently sensitive, so that the values derived afforded no evidence towards the question which has been elaborately studied by other authors[4]).

Years ago it has been demonstrated by A. Hantzsch[5]) that it is possible to test the constitution as well as the *purity of terpenes* by means of the *ultraviolet ray absorption.* A. Müller[6]) employed this method for examining citronellol, geraniol, and their derivatives. As the author communicates, it is sufficient, it is true, for obtaining the pure alcohols and their acetates to make use of the ordinary distillation process, whereas the purification of the cylic alcohols and their esters is said to be difficult. Unfortunately though, he furnishes but insufficiently the constants of the preparations under examination (the refractive index being nowhere recorded, and the optical rotation only in part) from which the purity of the preparations might have been judged. The solutions were prepared by means of optically pure alcohol. A citronellol obtained from Java citronella oil (b. p. 112.5 at 8 mm., d_{15° 0.8612, α_{D20° 2° 16′[7]) showed stronger absorption than a citronellol obtained from citronellal by reduction (b. p. 113.2° at 8 mm., d_{15° 0,8600, α_{D20° 4° 5′). A sample of geraniol (b. p. 108.2° at 9 mm., d_{15° 0,8836) purified from its calcium chloride compound[8]) showed a still lower absorption, and that of reuniol lay between that of citronellol and geraniol, but nearer towards the latter. With the acetates of the two alcohols the distance of the absorption curves was even larger. With the cyclic alcohols (cyclisation was performed by treating the esters with phosphoric acid at low temperature) the absorption bands approached each other the closer, the more the esters were subjected to fractional distillation. The purest preparations, *cyclo*-citronellol (b. p. 97 to 101° at 8½ mm., d_{15° 0.9023, α_{D20° 2° 30′[7]) and *cyclo*-geraniol (b. p. 96 to 98° at 11 mm., d_{15° 0.9462) showed but a feeble difference in the position of the absorption bands; with the cyclic esters, however, the differences were greater. The hydrogenated alcohols: — dihydrocitronellol (b. p. 113.5° at 15 mm., d_{15° 0.8565) and tetrahydrogeraniol (b. p. 116 to 117.5° at 14.5 mm., d_{15° 0.8621), with which the bands were located more towards the ultraviolet part of the spectrum, possessed nearly the identical absorption. Since likewise the results of the chemical examination indicated that in the hydrogenated alcohols the alkyl group occupied the same position, the alcohols proved to be *2*:*6*-dimethyl octanol-*8*.

With regard to earlier chemical investigation[9]), the author, basing on his optical examination, arrives at the conclusion that reuniol is merely a mixture of citronellol

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[1]) *Journ. Soc. chem. Industry* **38** (1919), 38 T; *Bericht* (German) **1920**, 101. — [2]) *Phil. Mag.* VI, **42** (1919), 633. — [3]) *Journ. f. prakt. Chem.* II, **102** (1921), 295. — [4]) Cf. *Bericht* (German) **1920**, 101. — [5]) Cf. *Report* April **1912**, 156. — [6]) *Berl. Berichte* **54** (1921), 1466. — [7]) The direction of the rotation is not stated. — [8]) In a paper published in the *Deutsche Parfümeriezeitung* dealing with the identical subject the author believes this calcium chloride compound to have been discovered in our laboratory. This is a mistake. This compound was first obtained by O. Jacobsen (*Liebig's Ann.* **157** [1871], 234. — [9]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. **364**. *Report* October **1904**, 119.

and geraniol (with at least 60 per cent. of geraniol), and that it must be struck off from chemical literature.

The absorption power of ultraviolet rays by various phenols and phenol ethers has been studied by Th. H. Durrans[1]. *Iso*eugenol proved to absorb ultraviolet rays much more than eugenol, and by methylating a phenol hydroxyl, *e. g.*, in *iso*eugenol, the absorption power for ultraviolet light is doubled. The absorption is likewise raised, in a still higher degree, by introducing the allyl side-chain, whereas by the propenyl side-chain the power of absorbing ultraviolet light becomes very small, as was shown by comparison of anisole, anethole, and methyl chavicol.

The investigation started by Rupe on the *influence of the constitution on the optical rotation* of active substances has been continued by A. Krethlow and K. Langbein[2]. In order to obtain further insight into the relation between rotatory dispersion and spectral absorption the authors examined such optically active substances as show marked or at least incipient, selective absorption of light in the neighbourhood of the visible spectrum as to their abnormal rotatory dispersion. Of 19 optically active bodies examined, six were perfectly normal in their optical behaviour, as they showed neither abnormal rotatory dispersion nor any selective absorption of light (amongst then camphorylidene-*β*-acetic acid methyl ester and camphoryl-*β*-acetic acid). Seven substances manifested anomalies in rotatory dispersion, amongst which were various menthyl esters, *e. g.*, of diacetoacetic and of pyruvic acids. Benzalcamphorylidene acetone and styrylbenzoylacetic acid menthyl ester behaved polarimetrically normal, but showed beginning spectral absorption.

The authors deduct from their investigations that a parallelism between abnormal rotatory dispersion and selective spectral absorption does not appear to exist. Amongst 33 bodies, only three (the white diphenylmethylacetoacetic and phenylbenzoylacetic acid menthyl esters, besides the pale yellow diphenylmethylal camphor) were found which showed both anomality in the rotatory dispersion and selective absorption of light[3].

F. Eisenlohr[4] reports on the molecular refraction of higher-melting bodies, and how the corresponding refractive indices are recalculated on the standard temperature of 20°.

A. Müller[5] observed *anisotropism* in the melting point of dianisal*cyclo*hexanone (prepared from pure *cyclo*hexanone and anisic aldehyde). At 160 to 161°, the body liquefied into an opaque mass which clarified suddenly at 171°. The phenomenon of voluntary spreading-out on water in a very thin film (long known with oleic acid and other bodies) has been observed by A. Marcelin[6] with a series of other substances. The experiments were carried out in the following manner: — When a small piece of camphor is floated on water, the surface of which was sprinkled with talc powder, one could observe how the talc grains were driven away from the camphor piece so that an empty circle was formed round the latter. The diameter of this "halo" reached a maximum depending upon the equilibrium ruling between the velocity of the dissolving of the thin camphor layer formed, and of the re-formation from the camphor piece. A series of photographs of this process was taken. From the area of the circle and the loss in weight of the camphor piece the thickness of the layer was calculated. Solid benzene (below 3° C.) showed the same phenomenon when floating on water.

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[1] *Perfum. Record* **12** (1921), 370. — [2] *Liebig's Ann.* **423** (1921), 324. — [3] Cf. *Report* **1918**, 96. — [4] *Berl. Ber.* **54** (1921), 2857. — [5] *Ibidem* 1481. — [6] *Compt. rend.* **173** (1921), 79.

When repeating the experiment with water on which oleic acid had been spread out previously, a halo was likewise formed, the diameter of which allowed of comparing the relative surface tension. Hereby the following figures resulted: — dimethylpyrolidone, 31.5; dimethylcampholic acid amide, 29.7; *iso*butylborneol (-camphol), 20,4; menthol, 20.4; *p*-toluidine, 16.7; camphor, 13; thymol, 12.1; borneol, 11.1; propylcamphocarbonic acid methyl ester, 9.4; benzal camphor, 0.94.

According to F. Hogewind[1]), nearly all odoriferous bodies, after long standing of their aqueous solution, show *colloid properties.* The odour was then found to be but slightly less intense than with the original oil; in addition, a layer of pure water, when poured carefully on such a colloidal solution, was found to assume the odour of the aromatic in question. These phenomena are readily explained by the well-known fact that the bodies mentioned show more or less the tendency to polymerise and resinify partly. In this process products are always formed which are far less soluble, and which, owing to the low concentration of the initial solutions, yield stable hydrosols.

A. Müller[2]) describes and recemmends an apparatus for determining the *viscosity* of essential oils termed "viscosostalagmometer". As years ago[3]) we established by way of experiment that the determination of this constant is of but little value when judging essential oils, we need not enter into a description of Müller's apparatus, which in its main features differs but slightly from the viscosimeters devised by Arrhenius, Ubbelohde, Engler, and others.

Botanical Notes.

Two *hybrids of spike and lavender* are described by M. Humbert[4]).

Hybrid A, growing up to 1 m. height, resembles in general habit and appearance a strong *L. latifolia* and is found here and there, more or less isolated, in the north of St. Saturnin-les-Apt at about 800 m. altitude, also near Buis-les-Baronnies about 400 m. altitude, in the Nyonais, and in the Causses. The flower stalks, divergent as in *L. latifolia,* generally bear in the axils of two higher leaves a pair of secondary flowering branches. At the base of the bushy, more or less interrupted inflorescences, often exceeding 10 cm. in length, the pairs of lower leaves form false rosettes. The bracts, in whose axils 6 to 12 flowers stand, remain green a long time even after flowering, at least in their upper part.

Hybrid B, whose height varies between 30 and 80 cm., resembles more *L. officinalis,* is found in great abundance throughout the entire zone of contact between *L. latifolia* and *L. officinalis,* often as numerous as the parents. The flower stalks are more or less divergent, generally simple, but sometimes bear in the axils of two higher leaves a pair of secondary branches. The lower leaves, approaching the base of the flower-bearing branches, form false rosettes but not so distinct as in *L. latifolia* or in hybrid A. The bracts are brown and membraneous after flowering. The slender inflorescence is 1.5 to 6 cm. long, usually not interrupted; 1 to 5 flowers stand in the axil of each bract.

The following characters are common to both hybrids: — 1. The flowering begins later than in *L. officinalis* and earlier than in *L. latifolia.* 2. The seeds are almost always sterile. 3. On bruising the plant a camphoraceous odour is noticed.

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[1]) *Archives néerland. de Physiol. de l'homme et des animaux* 5 (1920), 153. — [2]) *Chem.-Ztg.* 45 (1921), 759. — [3]) Cf. *Report* April 1901, 31. — [4]) *Perfum. Record* 12 (1921), 177.

Two other hybrids, A′ and B′, from *L. officinalis var. pyrenaica* and *L. latifolia*, correspond to the hybrids A and B described above. The species B′[1] resembling more *L. pyrenaica* and termed *L. aurigenara*[2] differs from hybrid B by the large size of its bracts. The more frequent hybrid A′ shows greatly developed bracteoles and an odour of camphor. Side by side with those hybrids there exist various other hybrid forms.

R. Laubert[3] gives a description of the most important *diseases of aromatic plants*, their origin and symptoms. Amongst the diseases known to occur with roses[4], the much-dreaded white rose-blight takes the foremost place. It is caused by a fungus belonging to the *Erysibaceæ*, *Sphærotheca pannosa*, (Wallr.) Lev. f. *rosæ*, and appears in shape of a white, dust- or flour-like deposit on the leaves, particularly on the tops of the young shoots. On the petioles and the calyces of the blossoms as well as on the fruits the white fur shows a coarse, fluffy appearance. Some rose varieties are attacked by this fungus but slightly, others are known to be very ready victims, *e. g.*, the Crimson Rambler. — Another rose fungus, *Phragmidium subcorticosum*, (Schrank) Winter (N. O. *Pucciniaceæ*) is recognized by its bright orange-red, oblong or round, pulvinate weals occurring in spring on the leaves, their stalks, and on other green parts. In the course of the summer, there may be found on the back side of the leaves small, light orange-yellow dusty pustules, at first only a few, but growing in number, which then turn black and sooty; on the upper side of the leaf, corresponding small yellow or reddish spots appear. Since the leaves attacked by this fungus turn yellow and fall off prematurely, the plants are seriously injured by this disease. The most of the high-class varieties known as remontant roses are readily attacked, in a less degree the tea hybrids and tea roses, whereas climbing and mountain roses are hardly ever afflicted. — The disease known as black spot blight *(Sternrusstau)* of the rose leaves occurs principally during damp weather and manifests itself on the upper side of the leaves in shape of round brownish-black or violet-black spots which on magnification prove to be composed of small dots and show a finely-radiated, fringed margin. The disease which likewise causes the leaves to fall off prematurely is generated by a fungus sponging upon the green leaves, *Actinonema rosæ*, (Lib.) Fries (N. O. *Sphaerioidaceæ*). Low-growing roses are preferably attacked by this disease. — The *Peronospora* disease of the roses is, on the whole, not very common, but at times rather dangerous. It can be recognized by small spots on the leaves, which occur irregularly and sporadically and are in the beginning yellowish-grey, later on yellowish-brown. The disease occurs sometimes with roses cultivated under glass and with rose seedlings and is caused by the sponging fungus *Peronospora sparsa*, Berk. (N. O. *Peronosporaceæ*). Some rose gardeners consider the disease caused by a fungus named *Coniothyrum Wernsdorffiæ* Laubert[5] (brown blight) to be the most dangerous of all rose diseases, since at times much damage is caused by this fungus. Early in spring, sporadic big round dark spots get visible on the green bark of the branches, particularly on the buds, which afterwards turn leather-brown to greyish-brown. Later on, the mortified bark splits up and peels off, whereby the woody interior gets visible. When the spot

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[1] As per a paper by J. Gattefossé (*Parfum. moderne* 14 [1921], 207) this hybrid was found in 1877 in the Pyrenees by Father Sennen and was termed *L. Senneni* by Abbé Coste. The hybrid *L. aurigerana*, Mailho, on the other hand, shows more the character of *L. latifolia* and would correspond to the hybrid A. — [2] In the *Index Kewensis*, a species *L. aurigerana*, Mailho is enumerated. — [3] *Deutsche Parf. Ztg.* 8 (1922), 1, 17. — [4] Cf. *Report* October 1915, 71. — [5] The so-called *Carcinoma rosæ*, recognizable by the abnormal extuberances, is generated not by the fungus *Coniothyrum Fuckelii*, but by lesions and action of the frost early in March. The fungus is but a secondary phenomenon. Cf. Sorauer, *Handbuch der Pflanzenkrankheiten*, 1921, vol. I. p. 658.

spreads round the branch the latter mortifies partly or totally. — The so-called *Botrytis* rot of the rose buds occurs in the summer when in the flowering time the weather is cool and damp. The rose buds, instead of opening, do not develop further, change colour and get covered with an ash-grey coating of the fungus *Botrytis cinerea,* Pers. (N. O. *Mucedinaceæ.*) Under favourable growing-conditions the plant is, in the most cases, not liable to suffer seriously by this fungus.

For combating these rose diseases the author recommends partly spraying with sulphurated substances, *e. g.,* powdered sulphur, solutions of calcium or potassium sulphide, &c., in case of *Sphaerotheca pannosa,* partly prophylactic treatment with sprays of copper preparations (copper-and-lime solution against *Phragmidium, Actinonema, Peronosposa* and other leaf fungi). Careful treatment of the roses, such as proper cutting and pruning, correct fertilization and tilling of the beds is likewise most essential.

About 35 different fungi have been found on the various species of mint, but only a part of them are parasites or cause diseases. Of the noxious fungi, the following may be mentioned. *Puccinia Menthæ,* Pers. (N. O. *Pucciniaceæ*), the very common mint rust, occurs in two chief forms, the uredo- or summer-spores, and the teleuto- or winter-spores. In summer time cinnamon-brown, wart-like, dusty pustules appear on the back side of the leaves, at first sporadically, afterwards in growing numbers, which constitute the stroma generating the unicellular summer (uredo) spores with pale yellow, short-bristled membrane. The uredospores communicate the disease in summer from leaf to leaf and from plant to plant. In addition to the brown pustules, largar black dust-like tubercles appear, the teleuto-stroma of the same fungus. They generate the oval, bicellular winter spores with a brown, wart-like membrane and long colourless petioles. When these teleutospores germinate in the next spring and form sporidia which infect the mint, the second, less common form of the disease develops in which the stalks and the petioles of the leaves acquire abnormal stoutness and are streaked by the mycelium of the rust fungus. The mint rust which occasionally causes deterioration of the odour of the plant and its oil, and often enough has destroyed the entire crop, is found not only on numerous species of *Mentha,* but also on various other members of the family *Labiatæ (e. g., Calamintha, Clinopodium, Origanum, Satureia).* However, not all the species an infected equally often or in an equal degree. For instance, *Mentha arvensis* is attacked by one of the eight different varieties of *Puccinia Menthæ* which does not or but slightly attack other species of *Mentha.* These biological properties must be considered when combating the rust disease. By raising the mint plantations in suitable uninfected soil the appearing of the disease can be warded off or at least its spreading can be limited.

Another disease, the so-called mint mildew, has been observed occasionally on *Mentha arvensis.* The green parts of the plants get covered with a white, flour-like coating which originates from an *Erysibacea, Erysiphe Galeopsidis,* D. C., or *E. Cichoracearum,* D. C. — The fungus *Septoria Menthæ,* (Thurm) Oud. causes the septoria spotted-leaf-disease of the mints which appears on the leaves of *Mentha arvensis* and perhaps also of other species in shape of black-lined, dark, later on light-grey spots. The mint septoria seems to be of minor importance. The same holds good for the following three diseases: — The ramularia spotted-leaf-disease (caused by *Ramularia menthicola,* Sacc. *[Mucedinaceæ]*) on the leaves of *M. silvestris, M. aquatica, M. canadensis, M. arvensis;* the physoderma weal disease of mints (caused by *Physoderma Menthæ,* Schroet. *[Cladochytriaceæ]* and characterized by blackish-brown callosities on the stalks and leaves of *Mentha aquatica*), and the synchytrium papillary disease of mints (caused by *Synchytrium aureum,* Schroet. *[Synchytriaceæ]*), golden-yellow nodules on the stalks and leaves of *Mentha aquatica*. The fusarium stalk rot, caused by the mycelium of *Fusarium Dianthi*, Prid et Del. and *F. roseum*, Meng. *(Tuberculariaceæ)*, which occurs occasionally in mint plantations is not quite as harmless as the preceding fungi. In this disease, the stalks turn blackish-brown at the base and wither. The following measures are recommended against this disease: — Destroying of all infected plants, suspending the cultivation of mints for several years, and, if necessary, disinfecting the soil.

Phytophysiological Notes.

With the object of studying the *process of formation*, in the plant, *of the essential oil*, J. Politis[1] investigated the secretory hairs of various labiatæ and geraniaceæ. In the secretory cells of the hairs, during the first stage of their formation, numerous oblong and twisted "chondriocontes"[2] are observable which contain a tannin compound. These "chondriocontes" widen gradually at each of their ends and separate thus that both from each a separate globule. These globules increase in size and pass over into the vacuoles of the cell where in course of time they are dissolved by the vacuole liquid. The content of the vacuole then shows feeble refractory power, and instead of the disappearing tannin, essential oil is formed[3].

E. Canals[4] investigated the influence exercised by *rays of varying wave-lengths* on the *formation of essential oil* in the plant. For this reason, the author transplanted young thyme plants grown in uncultivated land into pots and arranged them in boxes beneath ordinary (1), blue (2), or red (3) glass panes. After lapse of 20 days, all the plants in box (1) were in bloom, but showed pale blossoms, long stalks, and light green leaves. The plants in box (2) were like the former, some of them had faded away. In box (3), but a very few plants had attained a poorly blossoming stage, their stalks were excessive long and the leaves very broad. The thyme plants had entirely lost their xerophilous character. The oils distilled from the various plants showed the following percentage of thymol: —

Plants in box 3 (red glass) . . .	25.5 per cent. thymol
„ „ „ 2 (blue glass) . . .	36 „ „ „
„ „ „ 1 (ordinary glass) .	45 „ „ „
„ from open air	52 „ „ „

From these observations the author concludes that the thymol content of the oil decreases to the same extent as the plant loses its xerophilous character, and that the chemically active blue rays exercise an unfavourable influence on the formation of thymol which is far more marked with the calorific red rays.

The result of this study is in accord with earlier investigations and might have been expected. According to Lubimenko and Novikoff[5], light is indispensable in the formation of essential oil in the plant, but increased etiolation, at least within certain limits, raises the yield of oil. On the other hand[6], in most cases the rays of high

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[1] *Compt. rend.* **173** (1921), 98. — [2] The term "chondriocontes" is a newly-created one and is not to be found in the literature at our disposal. With "chondres" various species of granules are designed which occur in the nucleus and form the connections between the *linæ* in the frame. — [3] Already years ago, various scientists, *e. g.* Heckel and Schlagdenhauffen (*Compt. rend.* **114** [1892], 1291) favoured the theory that there exists some connection between the formation of essential oil in the plant and the tannins. — [4] *Bull.* Roure Bertrand Fils, April **1921**, 8. — [5] *Bull. applied Bot.* **7** (1914), 697. As per *Bot. Zentralbl.* **128** (1915), 696. The abstract on basil oil published in *The Amer. Perfumer* **10** (1915), 265, without mentioning the source, pertains to this paper by Lubimenko and Novikoff which we dealt with in our *Report* **1916**, 5. — [6] Pfeffer, *Pflanzenphysiologie*, 2nd ed. vol. II, p. 117.

refraction (blue to ultraviolet) exercise the same influence on the plant development as does weakened mixed light, while red and yellow light causes the same alterations in the plant as continuous darkness.

The emulsin obtained by aqueous maceration of almonds and precipitation of the extract with alcohol is a mixture of various enzymes containing, in addition to β-glucosidase (emulsin proper), lactase, gentiobiase, invertase, cellobiase, β-galactosidase, and other ferments. According to M. Bridel and R. Arnold[1]) it makes no difference in the preparation of emulsin whether ethyl alcohol, methyl alcohol, or acetone is employed. However, by varying the time during which the precipitant is allowed to act on the precipitate, emulsin preparations may be obtained in which some of the enzymes mentioned, *e. g.*, lactase or invertase, are missing.

Physiological and pharmacological Notes.

In an elaborate paper entitled, *Die Riechstoffe und das Riechen* (On aromatics and the sense of smelling), A. Tschirch[2]) discusses the hitherto-known investigations and theories on the physiology and chemistry of the sence of smelling published by Zwaardemaker, H. Henning, Rupe and Majewski, Marchand, Ruzicka, and others. Basing on these investigations and his own experience, the author endeavours to answer the question: — Which are the conditions which must be complied with in order that a body shows an odour? Tschirch arrives at the following results: —

1. The phase of the aromatic must show a certain temperature, and it is likewise of importance whether the aromatic is dissolved, and which is the solvent.
2. The substance must be readily soluble in air.
3. The distribution-coefficient for the aromatic and air must be favourable for air, hence in case of a mixture of equal quantities of aromatics the odour of such bodies will predominate which are most soluble in air.
4. The distribution-coefficient for aromatic + air ⟷ lipoid plasma of the olfactory cells must be favourable for the latter.
5. If it is assumed that chemical reactions are set up between the aromatic and the plasma, the former must contain atoms, atom groups, or ions which are able to react with the plasma molecules.
6. The osmophoric groups which generally are characterized by a strong tendency to react, are osmophoric only conditionally, at any rate only in cases when they are able to react with the colloidal plasm of the olfactory cells. The general chemical structure, more specially the building-up of the aromatic is of minor importance. A system of the shades of odour basing on the constitution of the various aromatics can not be established.
7. The sensation of odour is not caused by the aromatics, but by the very labile compounds formed in the colloidal olfactory cell-plasm (offering enormous surfaces) and mostly decomposing again instantaneously. These are either adsorption compounds — which is less probable —, or reaction-products between the aromatic (highly-ionised on account of its extreme dilution) and the olfactory cell-plasm which offers the aromatic a most extraordinary great surface in form of olfactory hairs, dimples, or conicles.

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[1]) *Journ. de Pharm. et Chim.* VII. **23** (1921), 161. — [2]) *Schweizerische Apotheker-Ztg.* **59** (1921), Nos. 17 to 20. From a reprint kindly forwarded to us.

8. These are the compounds exercising the sensation of odour on the olfactory nerve which is then conducted to the brain.
9. Hence, quite a series of conditions must be complied with in case that an odour is to be rendered perceptible. If one of them is not answered to and there is a missing link in the chain, no odour is noticeable.
10. Odour is a chemical action on the sense of smelling.

Tschirch speaks of the "solubility of the substance in air". In order to explain this, scientifically incorrect, expression we add that the author refers to a paper published by H. Erdmann[1]) who inferred, from the easy solubility of aromatics in *liquid* air, a specific solubility of there bodies also in *gaseous* air. For the sensation of smell, not the volatility of the substance is deciding, but a different property which Tschirch terms solubility in air. The author wishes to point out hereby that the molecule of the aromatic, which emits a different odour when in concentrated and in diluted state, undergoes changes due to the air. With increasing dilution a cleavage down to the ions is expected to pass off, as in the case of aqueous solutions.

F. B. Hofmann[2]) has published a paper on the sense of smell basing principally on self-observation. Owing to a severe catarrh of the nasal cavity the author had nearly entirely lost his power of smelling, and but quite by degrees and very slowly normal smelling sensation was recovered. During this period (several years), Hofmann undertook systematically a large series of experiments, the result of which is as follows: —

In the beginning Hofmann was only able to perceive the odour of natural and of artifical musk in their characteristic peculiarity and apparently also in their full strength. Pyridine smelled strong, but not so unbearable as usually. Of other bodies, the author had a sensation of odour with acetone and, quite indefinite as to character, of *iso*butyl and *iso*amyl alcohols. When in the following weeks the sense for smelling pyridine improved noticeably (the author made use of Zwaardemaker's olfactometer as modified by Zimmermann), also other substances which hitherto were odourless for him became noticeable. Ammonia and trimethylamine smelled strong; diethyl ketone, acetone, amylene hydrate, ether, and chloroform somewhat less strong; butyl and amyl alcohols, amyl acetate, butyrate, and valerate very weak, and thymol, toluene, and xylene extremely weak. Only a trace of odour was noticed, *inter alia,* with benzaldehyde, carvacrol, menthol, and phenol; yet Hofmann was able to differentiate between the odour of these bodies. No odour whatsoever was perceptible with asa fœtida, iodoform, mercaptane, scatole, and vanillin.

Some months later Hofmann noticed that many of the substances mentioned showed a strong smell, but quite different from their usual character. Normal behaviour was exhibited, in addition to musk, only by vanillin. Indole remained quite odourless. The author was particularly struck by the qualitative change in the different smelling sensations after their reappearing. Violets and ionone, for instance, smelled in the beginning like cigar tobacco, later on the true violet odour became perceptible.

Even several years afterwards the author failed to perceive some special odour characters. For him, putrefying albumen and scatole showed a faint sweetish odour, sulphuretted hydrogen, carbon disulphide, garlic, and various spices, such as caraway, an abnormal, indefinite smell.

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[1]) *Journ. f. prakt. Chemie n. F.* **61** (1900), 226. — [2]) *Zur Theorie des Geruchsinnes, I. Parosmie-Studien. Zeitschr. f. Biologie* **73** (1921), Nos. 1 to 4. As per a reprint kindly forwarded to us.

Hofmann concludes from his observations that most of the odoriferous substances act not only on a single, but on various peripheric receptive organs of different specific energy. Whenever a series of such receptive organs are acted upon and act together, combination smells are generated and the individual smells disappear more or less. The author considers this phenomenon to be the reason why some aromatics, when concentrated, show an odour different from that in diluted state[1]). By taking for granted that an odoriferous substances acts on several receptive organs it might be readily explained why the odours of many chemically pure substances resemble each other, and why from newly-synthesised bodies specific new odours result which otherwise are not to be found in Nature.

In a paper entitled, *Über einen historischen Beitrag zur Theorie der Geruchsempfindung* (On a historical contribution towards the theory of odour perception), H. Heller[2]) cites and discusses a passage from a book published, in 1814, by C. W. G. Kastner, professor of physics and chemistry in Halle, and entitled, *Einleitung in die neuere Chemie* (Introduction into modern chemistry). The author proves that already more than one hundred years ago Kastner held views on perception of odour which highly resemble modern theories. Nowadays, we agree with Kastner that the senses of taste and of smell are in close relation to each other, and also that in both cases it is necessary for the actual sensation that the respective active body be virtually present. Likewise, Kastner's opinion is correct insofar that we are only able to smell gases. We are unable to perceive liquid aromatics by their smell in case they are introduced into the nose. In Kastner's opinion, sensation of odour is due to a disturbance of equilibrium. This, too, is correct. On the mucous membrane of the nose, the content of water in the membrane and in the surrounding air, under normal conditions, are in equilibrium; however, as soon as the inhaled air carries particles of an aromatic, the conditions of osmotic and the chemical equilibrium are upset which makes the basis of sensual perception[3]). Finally, Kastner maintains that the sensation caused on the nasal mucous membrane is more unequivocal and less subject to errors than the sensation of sight. Heller agrees with this view (hitherto not contradicted) and supports it by proofs, the discussion of which, however, would carry us beyond the scope of our *Report*.

The same author[4]) demonstrates by various instances that chemical compounds which are generally said to show an offensive or unpleasant odour, when in a quite pure state, cause an entirely different and often even pleasant sensation of smell, sometimes, too, none at all. *Pure* acetylene, *pure* carbon disulphide, whose impurities show a putrid smell, show a pleasant ethereal odour. Likewise, various alkyl sulphides (*iso*amyl, ethyl sulphides), even ethyl mercaptane may be freed nearly entirely from their unpleasant smell by heating with copper powder (decomposition being but feeble); the latter adsorbs the evil smell. Hydrogen arsenide, whose garlic-like smell could be hitherto regarded as characteristic for that body, is according to Thoms and Hess[5]) odourless when quite pure, and when applied to the tongue causes a feeble sweet taste. (Of course these experiments were carried out with infinitesimal quantities.)

Heller points out that these facts have not received due consideration in some recent investigations, *e. g.*, in those of Kauffmann and of Henning on odour sensations. Hence, Kauffmann's[6]) theory of the change of odour (with alkylamines, mercaptanes,

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[1]) Cfr. the view held by Tschirch, preceding abstract. — [2]) *Deutsche Parfüm.-Ztg.* 7 (1921), 83. — [3]) Cf. for this the above-cited paper by Tschirch. — [4]) *Deutsche Parfüm.-Ztg.* 7 (1921), 123. — [5]) *Ber. d. deutsch. pharm. Ges.* **30** (1920), 488. — [6]) *Ztschr. f. Psychologie*, 2. *Abt.* **1908**, 217.

20632

thio-ethers, &c.) and likewise Henning's[1]) theory of compound odours which is based on the formula and the odour of (impure) carbon disulphide, are both untenable.

The connection between constitution and odour are dealt with in a paper by M. Guerbet[2]).

In research work on olfactology it is of importance to examine at any given moment the condition of the observer's sense-organ. According to H. Zwaardemaker[3]) this is done best (1) by establishing the accessibility of the nose to the air in respiration; (2) by testing the sensitiveness of the sense-organ. Whether the nasal cavities are normal or not can be ascertained, as the author proved years ago[4]), by breathing quietly and briefly on a metal plate held below the nose. From the shape of the two breathing-spots each subdivided by a hiatus conclusions may be drawn as to the transmissibility of the air through the nose. The acuity of the smell-organ is measured by means of the olfactometer, which contrivance we described as early as in 1904[5]).

By means of an improved type of olfactometer the author found the following limit values for a normal olfactory organ, expressed in tube-lengths for a just appreciable smell-sensation of the aqueous solutions: — concentrated solution of amyl acetate, 0.17 cm.; conc. sol. of nitrobenzene, 0.19 cm.; 0.08 per cent. sol. of terpineol, 0.23 cm.; conc. sol. of artificial musk (trinitro*iso*butyltoluene), 0.18 cm.; 0.11 per cent. sol. of (commercial) allyl alcohol, 0.26 cm.; 0.26 per cent. sol. of guaiacol, 0.20 cm.; 0.32 per cent. sol. of caproic acid, 0.15 cm.; 0.38 per cent. sol. of pyridine, 0.11 cm.; conc. sol. of skatole, 0.28 cm. For obtaining a general notion of the sensitiveness of the observer's nose, the nickel supply-cylinder may be replaced by a piece of new indiarubber tubing 10 cm. long with an interior diameter of 8 mm. An olfactory organ may be considered to be normal when its "minimum perceptibile[5])" for new, unused, vulcanised caoutchouc lies at about 1 cm. of the olfactometrical scale.

A *camera inodorata*, in which olfactometric experiments may be carried out regardless of any by-odours, has been devised by H. Zwaardemaker[6]). The camera is a box with glass walls of a capacity of 400 litres, the roof and the bottom being of aluminium. All wooden parts are equally covered with this metal which absorbs odorous matter but slightly. The box is placed on high legs, and the experimenter can pass his head from below through an opening that can be closed by a slide. The space may be rendered inodorous in a short time by means of an uviol or preferably a quartz lamp. But few odours are not destroyed by ultraviolet light. As the author demonstrated, in 1913, in conjunction with Tempelaar[7]), many odorous bodies are extremely sensitive to light, *i. a.*, many esters, acetone, chloroform, borneol, eucalyptole, eugenol, citral, terpineol, vanillin, coumarin, butyl alcohol, pyridine, skatole. Some odour of ozone which may, be present after the illumination disappears soon.

An olfactometer is attached under the slide at the bottom of the box, by which olfactometrical determinations can be made. By means of special contrivances, the inner tube of the olfactometer can be readily freed from any adhering scent. The observer must have closely-cropped hair and a quite scentless skin. If necessary, the skin must be thickly powdered with talc, or covered with odourless vaseline. After

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[1]) Henning, *Der Geruch.* Leipzig 1916. — [2]) *Journ. de Pharm. et Chim.* VII. 22 (1920), 344. As per *Chem. Zentralbl.* 1921, II. 414. — [3]) *Perfum. Record* 12 (1921), 308. — [4]) *Die Physiologie des Geruchs,* Leipzig 1895, p. 72. — [5]) Cf. *Report* October 1904, 104. — [6]) *Perfum. Record* 12 (1921), 243. — [7]) Cf. *Report* October 1913, 126.

this the observer remains in the box for five minutes (while the lamp radiates) with closed eyes screened by euphos-glass spectacles.

The experiments showed that in the *camera inodorata* the *minimum perceptibile* was on the average 25 per cent. lower than in ordinary surroundings.

The camera may be used also as a *camera odorata* by volatilizing a measured quantity of odorous substance and carrying out the olfactometric measurements in the scented atmosphere.

The firm of Lautier Fils, of Grasse, have constructed an appliance called "evapolfactometer" and designed for the recognition and valuation of odours. The apparatus was invented by Oddo[1]), and it consists of a thermometer, the mercury bulb of which is surrounded by an electrical resistance, and a very fine polished silver sheath. A rheostat above the thermometer permits of varying the current intensity, and hence the temperature. In use, the compound perfume liquid to be tested is poured on the silver rod and the temperature increased slowly. The separate odours are said to evaporate according to their degrees of volatility and may be perceived singly and one after another. This new process of analysing odorous bodies claims to offer various advantages over the usual method of testing by a spill of paper.

The sense of smell and the recognition of smells is rarely exercised and hence but feebly developed with most people. The following experiment was carried out at the Philadelphia College of Pharmacy and showed to which extent mistakes in recognizing smells occur even with skilled persons[2]). A series of 15 liquid odorous substances was submitted to twenty men, all with a more or less complete pharmaceutical training. The purpose of the test was to identify the odour of each specimen. Oil of turpentine was the substance which was best recognized, by all except three, which called it in turn, oil of anise, oil of caraway, and pine oil. Alcohol was difficultly recognized by the majority, on the other hand, vinegar[3]) was easily identified. Oil of cinnamon was reported by three persons as oil of anise, oil of bitter almond, and oil of wintergreen. Kerosene and gasoline were confusing to quite a number. Two men reported gasoline as chloroform, two others took kerosene for carbon disulphide. Creosote was judged by five as oil of clove, by five others as cresol. Only two men failed to identify methyl salicylate, who took it for oil of peppermint. Benzaldehyde was judged twice as nitrobenzene, oil of orange eight times as oil of lemon. One man took ether for ethyl nitrite. Linseed oil was recognized by nine persons, ten reporting it as fish oil or cod liver oil, and one taking it as neatsfoot oil. The identification of oil of nutmeg was not attempted by three of the men, three reported oil of turpentine, one reported it as oil of colander, and one as oil of cardamom. One of the students had no smelling sence for hydrogen sulphide and admitted that he detected only the most powerful odours.

On former occasions, we reported on the interesting investigations by K. von Frisch[4]) on the *sense of smell in bees*. The same author[5]) publishes now numerous new experiments on the "sign-language" of the bees. It could not be established beyond doubt whether the bees communicate by means of sounds; at any rate, however, the author was able to prove that the bees inform each other on the presence of food by some sort of sign-language. This communication is effected, in accord with the darkness in

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[1]) *Perfum. Record* **12** (1921), 135. — [2]) R. R. Foran, *Amer. Journ. Pharm.* **93** (1921), 683. — [3]) According to Weiss, vinegar acts not on the olfactory organ, but on the sense of touch. Cf. *Report* October **1915**, 70. — [4]) *Reports* **1917**, 121; **1919**, 108. — [5]) *Münch. med. Wochenschr.* **1920**, p. 566; **1921**, p. 509. As per a separate copy kindly forwarded to us.

the bee-hive, not by the sence of sight, but by touch. As soon as a bee (the collector) has discovered a food-place, it performs a "searching dance" when returned to the hive, which causes the others bees to swarm out in all directions and to search for the food-place. In cases where the crop emanates a blossomy smell the latter is noticed with the searching bee, and this smell is then traced. When the crop is abundant the collecting bee assists the others in searching by exhibiting its own smell-emanating organ (located between the 5. and 6. back segment of the body), and thus impregnating the surrounding of the food-place with its own smell.

About 40 essential oils have been investigated by Heinz1), of the Pharmacological Laboratory at Erlangen, with regard to their *pharmacological action.* Although the oils are frequently mixture of quite different components, they often show the same action, insofar as the latter is based upon identical physical properties of the oils, *e. g.*, volatility and solubility of lipoids. For instance, the odoriferous bodies have in common both the properties of local irritation, lasting, however, only a short time, and that of chemotaxis, *i. e.*, the attractive action on leucocytes. Owing to the solubility of the essential oils in lipoids, fats and oils, they easily permeate the skin protected by a layer of fat and hence assailable only with difficulty. Equally, the aromatics spread rapidly in the blood, since they combine readily with the blood corpuscles rich in cholesterol and circulate with them. Of details, Heinz deals with the action of peppermint oil on the liver2), of juniper oil on the kidneys, of thymol on the dental nerves, and of turpentine oil on the leucocytes. We content ourselves with this reference, as we have frequently reported on the pharmacological properties of these and of other essential oils3). Yet we wish to add that Heinz recommends an emulsion of milk with 5 per cent. turpentine oil for hypodermic injection, and that he introduces a powder for dressing wounds composed of sugar with 5 per cent. turpentine oil, which he terms "terpestrol".

J. C. C. Gunn and O. H. Plaut4) furnish some details on the *carminative action* of various essential oils, which, however, seem to contradict each other. According to Gunn, essential oils such as anise, peppermint, fennel oils, &c., when diluted 1 : 20000, stop the peristaltic motion entirely. The same action is effected by local application of 0.5 cc. of a solution of 0.05 per cent. of the oils in Ringer's solution. The therapeutic action consists in: relaxation of the cardia, alleviation of excessive peristaltic movements, besides local irritation, such as hyperæmia and sensation of heat.

On the other hand, Plaut noticed, with an isolated bend of a dog's bowel *(in situ)*, marked increase of the peristaltic motion. Previous treatment with atropine effected lessing of the motion, application to the bowel of cocaine neutralized the action completely, and morphine was without any influence on the action of the essential oils. No explanation is given for this discrepancy which may be caused by the method adopted, or by the different action of different doses.

A short paper by F. Marre5) deals with the use of aromatics as *sedative remedies.* Aromatics of animal origin, such as musk, civet, castoreum, and ambra are known ever since on account of their sedative action. Fumes of ambra were employed as a remedy for epilepsy, and later on inhalations of ambra were proved to possess an antispasmodic effect.

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1) *Münch. med. Wochenschr.* **68** (1921), 628. As per *Deutsche Parf. Ztg.* **7** (1921), 157. — 2) Cf. *Bericht* (Germ. ed.) **1921**, 38. — 3) Cf. our *Reports* under the heading *Pharmacological and physiological Notes.* — 4) *Journ. pharm. and exper. Therap.* **16** (1920), 39 and 311. As per *Therap. Halbmonatsh.* **35** (1921), 184. — 5) *Parfum. moderne* **14** (1921), 80.

Of odours of vegetable origin showing a sedative action, the author enumerates the lily, lily of the valley, carnation, orange, opopanax, vanilla, and heliotrope. Various blossoms, such as the lily, tuberose, and honeysuckle, are known to exercise a stupefying action; by experimenting on animals the essential oils were proved to possess, with the living organism, a similar action as chloroform or ether[1]).

Sores of various kinds have been treated in sixty-eight cases successfully with terpeneless oil of lavender[2]). If the greater part of the infected sores show no inflammatory symptoms after several applications of the pure oil, it is then desirable to resort to weaker solutions (1 to 10 per cent.). Gangrene was arrested immediately, and in many instances cicatrisation was complete in less than a month. In the case of varicose ulcers in particular, a weak solution has proved an excellent antiseptic. Very good results were obtained particularly with burns and scalds by the application of the terpeneless oil for four or five days, followed by wet dressings during four or six days, and finally dressing with starch powder or bismuth. In the case of chancrous sores, the pure oil was applied, and then a powder of thymol iodide and dry dressing. In other cases, after removing the pus, the pure oil was injected and the sore covered with a pad damped with the oil; this was renewed daily, and finally a dry dressing applied after cleansing the sore.

G. and K. Cori[3]) report on the treatment of febrile tuberculosis of the lungs with intramuscular injections of *menthol + eucalyptus oil.* The authors injected two to three times a week 0.5 to 1.0 cc. of the following mixture: — 0.1 g. iodine, 0.5 g. camphor, 10.0 g. menthol, 10.0 g. eucalyptus oil, 20.0 g. castor oil, and give the result of the treatment of 168 poor or indigent patients as follows: — *(a)* Patients with tuberculosis of the second and third stage, as well as infantine tuberculosis, can in many cases be freed from fever by means of Berliner's mixture[4]), so that they mostly may undergo a treatment with "alt-tuberculin" without contracting fever. *(b)* The suppression of fever passes off lytically and without unpleasant consequences of any kind. *(c)* If during a tuberculin-treatment continual fever occurs, injections according to Berliner enable further application of tuberculin by depressing the fever. *(d)* Regardless of the lowering of the fever, the subjective complaints, such as pain, cough, or night perspiration, &c., were in all cases alleviated or even removed. *(e)* A rise in temperature after injections of tuberculin have no bad influence upon the action of tuberculin in the second stage of pulmonary tuberculosis, whereas in the third stage a rise in temperature is generally associated with loss in weight, hemoptœa, &c. *(f)* The fever-depressing action of the Berliner mixture passes off by action on the pulmonary seat of the disease as being the cause of the fever. This was proved by experiments which demonstrated that during the treatment with the Berliner mixture the cutaneous sensitiveness towards tuberculine showed a decrease.

As has been shown by Macht[5]), the *antispasmodic action* of the combined opium alkaloids is due to the presence of the benzyl nucleus in the alkaloids of the papaverine group. Simpler compounds containing the benzyl nucleus, such as benzyl alcohol, some of its esters, and benzaldehyde, but not benzoic acid, have the same action. The antispasmodic properties are exhibited, as is demonstrated by H. A. Shoule

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[1]) Detailed studies on the after-effects on, and poisoning of, the olfactory sense have been published also by Henning. Cf. *Report* **1916**, 103. — [2]) Marchand, *Perfum. Record* **12** (1921), 153. — [3]) *Therap. Halbmonatsh.* **35** (1921), 236. — [4]) Cori's recipe differs somewhat from the prescription given originally by Berliner. — [5]) *Journ. of Pharmacol. and exp. Therap.* **9** (1917), 287; **11** (1918), 263.

and P. Q. Row1)), in a higher degree by veratryl and piperonyl alcohols, piperonal, vanillin, veratryl aldehyde, and *o*- and *p*-hydroxybenzaldehyde.

Since nothing is known as to the therapeutic action of the benzyl esters of the higher fatty acids and the aliphatic and aromatic amino-acids, and other sulpho and amino-acids, the authors prepared a number of these esters, and determined the physical and therapeutical properties. The esters of the higher fatty acids were tasteless, colourless liquids — those of the unsaturated acids showed an unpleasant taste — or low-melting solids, which had neither an anesthetic effect nor an irritating action on the mucous membrane. Owing to the insolubility in water of these esters the usual physiological tests on animals were not entirely satisfactory. Clinical tests were therefore resorted to, which demonstrated the antispasmodic action of these esters in asthma, dysmenorrhœa, high blood pressure, pylorospasm, and spastic constipation.

The benzyl esters of *p*- and *m*-amidobenzoic acid showed an irritating effect on the mucous membrane and possessed local anesthetic properties.

Benzyl lactate was also prepared but because of its irritating effect it was not tested clinically.

The benzyl esters of mixtures of fatty acids derived from natural fats had the equal therapeutic properties as the benzyl esters of the individual fatty acids. They are more readily hydrolysed by lipase than are the benzyl esters of aromatic acids.

As C. Nielsen and J. A. Higgins2) have observed, the *peristaltic movements* (observed *in situ* with dogs) are lessened by intravenous infection of a 5 per cent. emulsion of benzyl benzoate or cinnamate. The latter ester is at least quite as effective as the benzoate, but is not quite so effective in lowering the blood-pressure. Benzyl cinnamate shows a moderately toxic action; a small dog stood about 15 gms. after oral application without any harm.

Fröhlich and Grossmann3) continued their experiments on the medicinal *action of camphor*4). A frog's heart, when under camphor treatment, reacted no more, on application of alternating current, by raging *("wühlen")*. The authors conclude herefrom that camphor is capable of improving the metabolism of the heart ventricle.

G. Joachimoglu5) was able, by application of camphor to a leech preparation, to effect increase of the tonus, and contractions of hours' duration. *D*-, *l*-, and *d,l*-camphor showed the same action. Since thymol, of anthelminthic fame, causes a similar effect, the author believes camphor to be efficacious as vermifuge when applied as enema.

Terpichin (a solution of 15 per cent. turpentine oil with each 0.5 per cent. of quinine and anesthesine in olive oil) is used for *dermatological purposes* and with various inflammations. W. Karo6) prefers the intravenous injection of this remedy in lieu of the usual intragluteal application, since it proved to be superior to the latter.

Trabut7) recommends in the *treatment of diabetes* a decoction of eucalyptus leaves (10 to 15 gr. to a litre of water and boiled down to one-half of its volume). The leaves of *Eucalyptus diversicolor* and *E. rostrata* act as well as those of *E. Globulus*.

As to the medicinal use of *turpentine oil*, see p. 77 of this *Report*.

On injections with solutions of *benzyl benzoate*, vide p. 92 of this *Report*.

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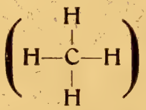
1) *Journ. Amer. chem. Soc.* **43** (1921), 361. — 2) *Journ. of laborat. and clin. med.* **6** (1921), 388. As per *Chem. Zentralbl.* **1921**, III. 1173. — 3) Cf. *Bericht* (Germ. ed.) **1921**, 63. — 4) *Arch. f. exp. Pharm. u. Path.* **89** (1921), 1. As per *Therap. Halbmonatsh.* **35** (1921), 376. — 5) *Arch. f. exp. Pharm. u. Path.* 88 (1920), 364. As per *Therap. Halbmonatsh.* **35** (1921), 376. — 6) *Klin. Wochenschr.* **1** (1922), 89. — 7) *Perfum. Record* **12** (1921), 265.

Chemical Notes.

In a paper entitled, "Some constituents of essential oils and their structural relations", J. W. D. Hackh1) endeavours to give an outline of the structural relation of the above-mentioned constituents, and to illustrate by practical application the advantages of structure symbols, the new chemical notation of organic compounds, the present method of notation occupying a vastly greater space and annoying the printer in a high degree. The old formulæ are replaced by geometrical devices which eliminate the customary symbols C, H, O, N and represent their atoms by points from which one, two, three, or four lines, respectively radiate. A straight line — stards for hydrogen (H—H, assuming one atom of hydrogen at either and of the stretch), an angle > represents water $\left(\begin{matrix}H\\H\end{matrix}\!\!>O\right)$, the sign —< stands for ammonia $\left(H-N\!\!<\!\begin{matrix}H\\H\end{matrix}\right)$, and a cross +, for methane



$$\left(\begin{matrix} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{matrix}\right)$$

. Where two stretches meet, one atom of oxygen is located, where three or four meet, an atom of nitrogen, or carbon, respectively. Each organic compound belongs to a different type and a different class, such as hydrocarbons (o—, or R—H, the circle standing for the radical), alcohols (o—>, or R—OH), aldehydes (o-ρ, or R—CHO), &c. The type of the compound indicates its chemical character and reactivity, the class its general structural characteristics, either saturated or unsaturated, aliphatic or aromatic. Expressed by the new notation, ++ stands for ethane $CH_3—CH_3$,

for ethylene $CH_2=CH_2$,

for hexamethylene C_6H_{12},

for benzene C_6H_6,

for menthane, and

for camphor, &c.

These examples seem sufficient to give the reader an idea of Hackh's notation. Those who are interested in the study of the new system may resort to the original paper, where the notation of 157 compounds occurring in essential oils is given and their structural relation is detailed.

The salts of the higher fatty acids, when in solution, crystallise in the shape of a spongy mass which, according to C. A. Cofman-Nicoresti3), shows a great power for absorbing volatile oils. As little as 5 per cent. of the salts was sufficient for obtaining such "solid solutions".

Hydrocarbons.

A process for obtaining *aromatic hydrocarbons* has been devised by A. S. Ramage3):— Hydrocarbons containing one or more alkyl groups are treated, in the presence of a catalyst, such as ferrous oxide, with hydrogen. The alkyl groups are hereby replaced by hydrogen.

A process for the preparation of *polycyclic hydrocarbons of the terpene series,* for which a patent is applied by the firm of Schering, of Berlin4) consists in heating the

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1) *Journ. Amer. pharm. Ass.* 9 (1920), 948. As per a separate copy kindly forwarded to us. — 2) *Chemist and Druggist* 95 (1921), 854. — 3) Am. Pat. 1365849 of Jan. 18th, 1921. As per *Chem. Zentralbl.* 1921, II. 558. — 4) Germ. Pat. Appl. C/29518, published Jan. 12th, 1922.

hydrazones of terpene ketones with mercuric oxide, or the double salts of mercuric chloride and the hydrazones, after addition of the equivalent amount of alkali, in an indifferent solvent. By the interaction of the mercuric oxide and the hydrazones, difficultly-soluble basic mercury compounds are formed whose constitution possibly resembles that of the mercuri-ammonium compounds and which decompose, on heating in indifferent liquids, according to the following equation:—

$$C_{10}H_{16}:N\cdot NH\cdot Hg\cdot OH \longrightarrow C_{10}H_{16} + N_2 + Hg + H_2O.$$

The patent specification contains details for the preparation of tricyclene from camphor hydrazone (crude yield, 78.3 per cent.), of d-*cyclo*fenchene from *d*-fenchone hydrazone, and of *apo*cyclene from camphenilone hydrazone.

The principal products resulting from the pyrogenetic decomposition of *benzene* are, according to E. Peytral[1]), hydrogen and diphenyl; $2C_6H_6 \longrightarrow C_6H_5\cdot C_6H_5 + H_2$. One-third of the hydrogen formed results either from a radical decomposition of part of the benzene into methane, carbon (graphite), and hydrogen, or (as is more probable) from a part of the diphenyl formed and then decomposed further.

Benzaldehyde, when submitted to the treatment indicated, decomposed principally into benzene and carbon monoxide, besides into diphenyl, carbon monoxide, and hydrogen. In addition, a small amount of anthracene is formed due to condensation in the hydrogen atmosphere. As secondary products of the decomposition of diphenyl, carbon and methane were traced.

A process for obtaining p-*cymene* from the waste terpenes (b. p. about 175°) resulting from the camphor synthesis, or the fractions boiling at 175° and at 160° of Swedish or Polish "turpentine" (pine) oils has been published by the Rheinische Campherfabrik[2]), of Düsseldorf. The respective fractions are chlorinated slowly at temperatures ranging from 10 to 80°, the reaction-product distilled with steam, the volatile oil heated with some zinc chloride and subjected to distillation. Yield about 60 per cent. of the primary material; it may be raised to 75 per cent. by heating the crude material with an inorganic or organic acid, or an acid salt, and by using the fraction boiling at 175° for the chlorination.

Ralph H. McKee and Leland J. Lewis[3]) recommend *fat-splitting reagents obtained from cymene, i. e.,* cymene stearosulphonic acid. The compound is obtained analogous to Twitchell's[4]) method for preparing aromatic stearosulphonic acids. 280 gr. of oleic acid and 140 gr. of cymene were stirred, and 300 gr. of sulphuric acid (66 deg. Bé.) was gradually added, keeping the temperature below 35°. Further details on the preparation and purification of the product may be gathered from the original paper.

On comparison with Twitchell's reagent, benzene and naphthalene stearosulphonic acids, and the "Kontakt" reagent, the cymene derivative offers, in the opinion of the authors, the following advantages:—It is more easily and cheaply made and can be produced as a uniform product. The fatty acids as well as the glycerin obtained by its use are both of a lighter colour.

Terpinene.—Contrary to the other nitrosites of unsaturated bodies, whose structure is mostly bimolecular, the nitrosite of terpinene possesses the simple molecularity of $C_{10}H_{16}O_3N_2$, and it does not show the colour reactions characteristic of the dissociation

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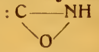
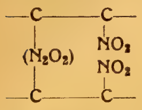
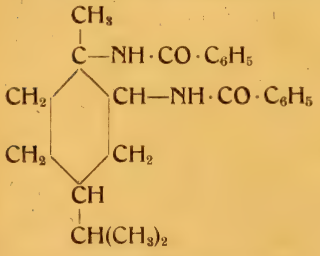
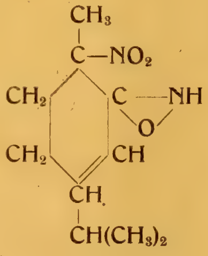
[1]) *Bull. soc. chim.* IV, 29 (1921), 44. — [2]) Germ. Pat. 819162 and 319163, July 14th, 1921. Engl. Pat. 156329, Febr. 3rd, 1921. — [3]) *Americ. Perfumer* 16 (1921), 175. — [4]) *Journ. Americ. chem. Soc.* 22 (1900), 22.

of the bisnitroso group. Since, however, the nitrosite, on treatment with caustic potash, gives rise to a body $C_{20}H_{31}N_3O_4$ (m. p. 163 to 164°), and since it interacts with amines, with formation of nitrolamines —C(:NOH)—C(·NHR)= and splitting-off of NO_2H, Wallach[1] at a time was of opinion that terpinene nitrosite is bimolecular, at least in the solid state, and that the grouping NO_2 was attached to the carbon atom by the usual nitrite-linking C—ONO, as in the genuine nitrosites. This view is not shared by H. Wieland and F. Reindel[2]. The behaviour of di*cyclo*pentadiene and of ethylene shows that on addition of nitrogen trioxide N_2O_3 to unsaturated bodies *pseudo*nitrosites (*bis*nitroso-nitro compounds) are formed, of the structure as given by the annexed formula. Equally terpinene = $\Delta^{1,3}$-dihydrocymene containing a grouping of two conjugated double-bonds, is no exception to this rule. By catalytic hydrogenation of terpinene nitrosite (m. p. 153 to 154°), Wieland and Reindel obtained, besides a monovalent base, a diamine which was found to be 1,2-diaminohexahydrocymene and which was identified by its dibenzoyl compound (I, m. p. 165°) and the hydrochloride of the monobenzoylated diamine (m. p. about 290°, turning brown). Hence, terpinene nitrosite undergoes a partial reduction to 1,2-diaminohexahydrocymene, and both the NO- as well as the NO_2-group are linked to the carbon atom by their nitrogen. By this reaction the structured formula (II) is established beyond doubt, where the authors have replaced the :C:NOH-group by the group  in order to indicate the insolubility in alkali. The interaction with alcoholic potash studied by Wallach[3] and yielding the nitrite must be considered to be an intramolecular alkylation, and formula (III) must be attributed to the reaction product. The body $C_{10}H_{15}O_6N_3$ obtained by Amenomija[4] by action of nitric acid on terpinene nitrosite is, in the opinion of the authors, 1,2,2-trinitrotetrahydrocymene.

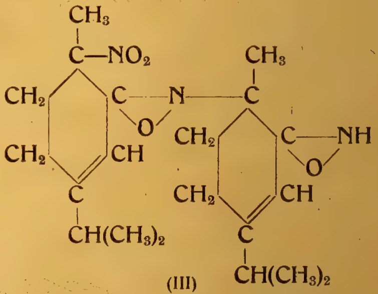




(I) Dibenzoyl-1,2-diaminohexa-hydrocymene.



(II) Terpinene nitrosite.



(III) Reaction product from terpinene nitrosite.

On *moslene*, see p. 51 of this *Report*.

Verbenene. — In a prior publication, Blumann and Zeitschel[5] had proved that verbenol (I) splits off water readily on treatment with acid reagents and yields a doubly-unsaturated bicyclic terpene $C_{10}H_{14}$, verbenene. The authors prove now[6] that verbenene, which is isomeric with *p*-cymene and which can be transformed into that terpene, possesses the structure of a dehydro-*α*-pinene (II). By oxidation by means of alkaline permanganate solution, verbenene was degradated to *cis*-norpinic acid (III) by which the intactness of the tetracyclic system was proved. The conjugated position of the

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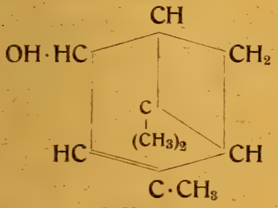
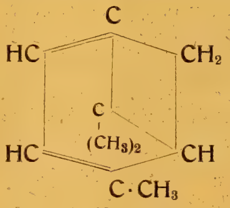
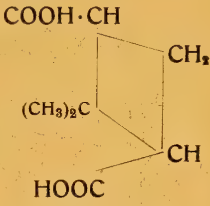
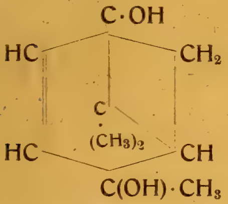
[1] *Liebig's Annalen* **356** (1907), 223. See also *Report* April **1907**, 142. — [2] *Liebig's Annalen* **424** (1921), 92. — [3] *loc. cit.* — [4] *Berl. Berichte* **38** (1905), 2020. — [5] Cf. *Report* October **1913**, 105. — [6] *Berliner Berichte* **54** (1921), 887.

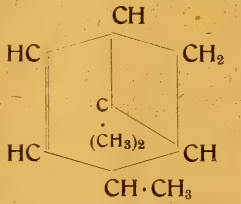
double bonds was proved by the formation of the terpene from verbenol (I), by the value found for the molecular refraction (44.57, calc. for $/\overline{_2}$ 43.05), and by the behaviour of verbenene towards bromine. The easily-obtainable dibromide was strongly optically active, the rotation being opposite to that of the primary material, and gave rise, on treatment with dilute potash solution, to an unsaturated glycol $C_{10}H_{16}O_2$ (IV; m. p. 141°) and to an apparently oxide-like body which was not examined further. The authors were unsuccessful in trying to replace the bromine atoms by hydrogen. On the other hand, dihydroverbenene (V; b. p. 158 to 159° [726 mm.]) was formed on treating the terpene with sodium and alcohol. (Cf. Semmler, On the reduction of α-phellandrene, *Berl. Berichte* **36** [1903], 1035 and 1753.) Dihydroverbenene, which may be taken for a δ-pinene, strongly resembled α-pinene in its physical and chemical properties, such as the formation of pinene hydrochloride on introducing dry hydrogen chloride, or of a nitroso body identical with nitrosopinene from the nitrosochloride. Hence the authors believe that α-pinene is primarily formed by the action of acid reagents.

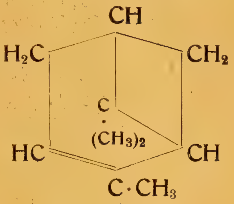

(I) Verbenol.


(II) Verbenene.


(III) Norpinic acid.


(IV) Glycol from verbenene dibromide.


(V) Dihydroverbenene, δ-pinene.


(VI) α-Pinene.

Pinene. — By repeated fractional distillation, *in vacuo,* of 15 litres of French turpentine oil, Pariselle¹) obtained: — α-pinene, b. p. 153.5 to 154.5° (760 mm.), or 62° (32 mm.), d_{0° 0.8748, $[\alpha]_{D15^\circ}$ — 43,48°, n_{D13° 1.4690, rot. disp. 1 ($\lambda = 589$), 1.185 ($\lambda = 546$), 1.44 ($\lambda = 492$), 2 ($\lambda = 436$), coefficient of viscosity 0.0141, mol. refr. 43.85, and β-pinene, b. p. 163 to 164° (760 mm.), or 71.5° (34 mm.), d_{0° 0.8848, d_{15° 0.8728, $[\alpha]_{D15^\circ}$ — 19.80°, rot. disp. 1 ($\lambda = 589$), 1.1 ($\lambda = 546$), 1.15 ($\lambda = 492$), 1.08 (?) ($\lambda = 436$).

With hydrogen bromide, α-pinene yielded the solid pinene hydrobromide, m. p. 94°, b. p. 94° (12 mm.), $[\alpha]_{D15^\circ}$ + 27.95° (in toluene solution), and a liquid hydrobromide which contained the solid isomeride in the dissolved state. β-Pinene showed exactly the same behaviour and gave a solid monohydrobromide with nearly the identical physical constants, except $[\alpha]_{D15^\circ}$ being — 31.50°. By the action of bromine on α-pinene Pariselle obtained the solid monohydrobromide, a liquid monohydrobromide, a dibromide (m. p. 150°, with slight decomposition at 130°), and Wallach's dibromide (m. p. 166 to 168°)²).

By synthesising pinocamphone and α-pinene from monocyclic bodies, L. Ruzicka and H. Trebler³) were able to prove the correctness of Wagner's pinene formula (I),

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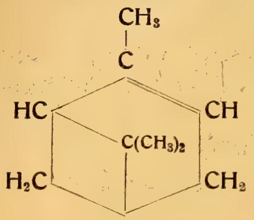
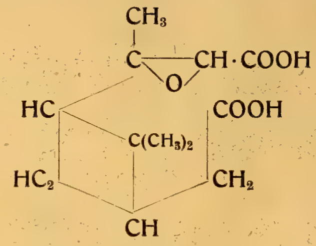
¹) *Compt. rend.* **172** (1921), 1496. — ²) Cf. *Liebig's Annalen* **264** (1891), 7. — ³) *Helv. chim. acta* **4** (1921), 666.

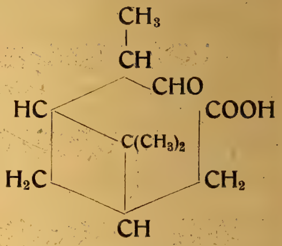
which hitherto was not quite fully established. By condensing the ethyl ester of pinonic acid with chloroacetic ester according to the method devised by Darzens[1]) the authors obtained the corresponding glycidic dicarboxylic ester and thence by saponification the acid itself (II; m. p. 128° with evolution of carbon dioxide). When this acid was heated to 230° it splitted off carbon dioxide and passed over into homopinocamphoraldehydic acid (III; b. p. 130 to 140° [3 mm.]; semicarbazone, m. p. 193 to 194°) which on oxidation with permanganate yielded homopinocamphoric acid (IV; diethyl ester, b. p. 130° [1 mm.]). This acid was best transformed into pinocamphone (V) by the method of W. Dieckmann[2]),



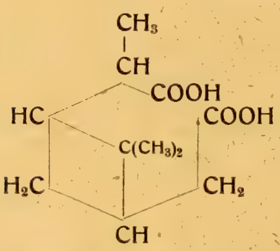
(I) Pinene.



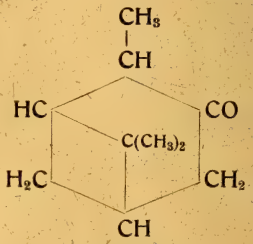
(II) Glycidic dicarboxylic acid from pinonic acid.



(III) Homopinocamphor-aldehydic acid.



(IV) Homopinocamphoric acid.



(V) Pinocamphone.

by condensation of the diethyl ester of the (IV), in xylene solution, with sodium. The ketonic acid ester formed primarily was saponified, with formation of pinocamphone, by boiling with a 15 per cent. hydrochloric acid. The semicarbazone and the oxime of the *d,l*-pinocamphone thus obtained were identical (as was proved by the melting-point of the pure substance and of the mixture) with the corresponding preparations of Wallach[3]) resulting from a *d,l*-pinocamphone from nitrosopinene by treatment with zinc and acetic acid. Since pinocamphone may be transformed into pinylamine and α-pinene by means of the reactions described already by the authors[4]), an uninterrupted way is given for the partial synthesis of α-pinene from α-pinonic acid.

Hitherto it has been generally taken for granted that on addition of dry hydrogen chloride to pinene always pinene hydrochloride = bornyl chloride (I) is formed. O. Aschan[5]) proved this assumption to be incorrect, as the isomeric liquid, *tertiary* pinene hydrochloride is formed in this reaction. This compound, stable only at a temperature below —10°, partly splits off hydrogen chloride on treatment with aniline and yields pinene rotating in the same sense as the starting material. When the tertiary pinene hydrochloride is removed from the freezing mixture, it rises in temperature up

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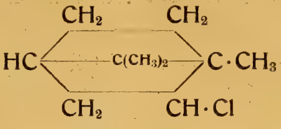
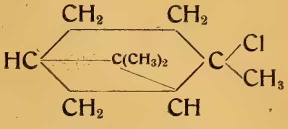
[1]) *Compt. rend.* **139** (1904), 1214. — [2]) *Liebig's Annalen* **317** (1901), 27. — [3]) *Ibidem* **304** (1898), 287. — [4]) Cf. *Bericht* (Germ. ed.) **1921**, 106. — [5]) *Vetenskaps Akad. Förhand.* 67, part A. **1914**, No. 1. As per *Chem. Zentralbl.* **1921**, III. 629.

to 60 to 80° and rearranges itself to solid bornyl chloride. It is probable that whenever bornyl chloride is formed from pinene and hydrogen chloride, the unstable compound (III) is always formed intermediarily.



(I) Bornyl chloride.

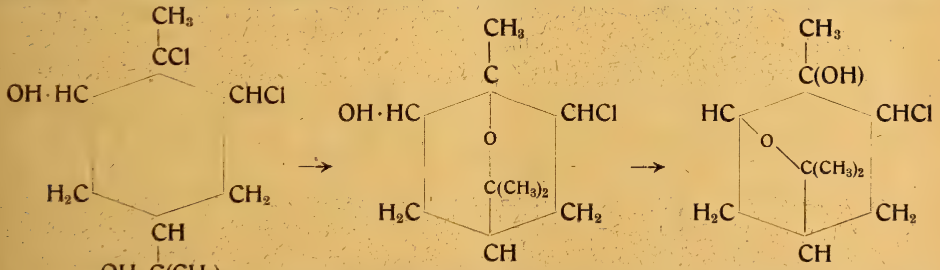


(II) Tertiary pinene hydrochloride.

Nopinene, when submitted to the same treatment, equally gave rise to the identical tertiary pinene hydrochloride which with aniline passed over into pinene and not into nopinene. Since with the tertiary chloride the velocity of its rearrangement, at 0°, exceeds its formation velocity from pinene and hydrogen chloride, it was not possible, even at a low temperature, to obtain it free from bornyl chloride. Its odour is strangely suffocating, and it attacks the mucous membranes. The mixture of hydrocarbons obtained on scission with aniline consists mainly of pinene, but contains also some dipentene, or limonene, and a still unknown cyclic terpene (in the fraction b. p. 162 to 167°).

The action of hypochlorous acid on pinene, examined years ago by Wagner[1] and his collaborators, has been investigated afresh by G. G. Henderson and J. K. Marsh[2]. These authors found that the products obtained formerly, two chlorohydrins, pinol oxide, sobrerythritol, and nopinol glycol, are not the primery products of the reaction, but are formed from these by the action of the potassium hydroxide employed. Treatment of pinene (b. p. 156 to 157°) with a very dilute aqueous solution of hypochlorous acid yielded two crude products of which the one was soluble in water. This product was a mixture of three crystalline dichlorohydrins, $C_{10}H_{18}O_2Cl_2$, which melted at 139 to 140°, 124 to 126°, and 155° respectively, together with a viscous, oily substance. The first of these dichlorohydrins (nitrobenzoate, m. p. 175°) gave reactions identical with those of the compound (m. p. 136°) prepared by Wagner and Slawinski. By direct synthesis of sobrerol dichloride (*cis*-1,2-dichloromenthane-6,8-diol, m. p. 138°) from *i*-sobrerol the authors confirmed Wagner's view that pinene dichlorohydrin (m. p. 139°) and sobrerol dichloride (m. p. 136°) are identical. (The mixture of both bodies showed the same m. p. 138°).

On treatment with two molecules of aqueous caustic potash, the dichlorohydrin (I), m. p. 139°, formed pinol oxide and *i*-pinol glycol-2-chlorohydrin (III) $C_{10}H_{17}O_2Cl$ (m. p. 104 to 105°) which after heating with caustic potash solution gave rise to pinol oxide. An isomeric, but entirely different chlorohydrin $C_{10}H_{17}O_2Cl$ (m. p. 70 to 71°; nitrobenzoate, m. p. 125°) was formed on shaking one mol. of the dichlorohydrin (m. p. 139°) with one mol. potassium oxide in a very weak aqueous solution. This body was readily transformed, by the action of water, into *i*-pinolglycol-2-chlorohydrin, m. p. 104°. It may



(I) Pinene dichlorohydrin (m. p. 139°). (II) Isomeric intermediary (?) product, chlorohydrin (m. p. 70 to 71°). (III) Pinolglycol-2-chlorohydrin (m. p. 104°).

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[1] Cf. *Reports* October 1896, 88; October 1899, 63. — [2] *Journ. chem. Soc.* 119 (1921), 1492.

be assumed that the compound of the m. p. 70 to 71° results as an intermediary product in the preparation of pinolglycol-2-chlorohydrin from pinene dichlorohydrin (m. p. 139°).

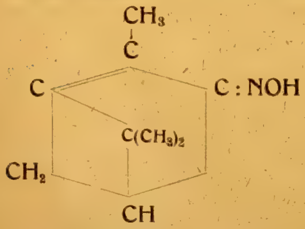
The dichlorohydrin of the m. p. 124 to 126° was optically active ($[\alpha]_{Hg}$ — 28,2°) and was apparently 2,8-dichloromenthane-1,6-diol. With dilute aqueous potassium hydroxide it yielded optically active pinolglycol-2-chlorohydrin (m. p. 131°), some *i*-pinolglycol-2-chlorohydrin (m. p. 104°), and a trace of pinol oxide. The third dichlorohydrin, m. p. 155°, was present only in a very small quantity and was likewise optically active ($[\alpha]_{Hg}$ — 59.5°); it is perhaps a derivative of β-pinene, a little of which may possibly have been present in the pinene used.

The viscous, oily body (see above), when treated with a 10 per cent. potassium hydroxide solution, yielded pinolglycol (m. p. 124°), which was evidently formed from pinol oxide and furthermore from a dichlorohydrin.

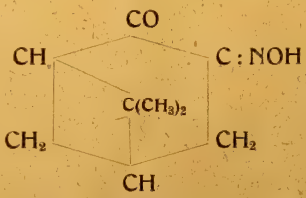
Fractional distillation *in vacuo* of the oily primary product which remained undissolved in water yielded, besides some unchanged pinene, some tricyclene dichloride, $C_{10}H_{16}Cl_2$, m. p. 169 to 172°, identified by conversion into camphane, m. p. 154 to 155°.

In a third paper on pinene[1]), L. Ruzicka and R. Trebler[2]) were able to disprove the formula (I) for *nitrosopinene*, as suggested by Wallach[3]). It had been Wallach's intention to explain, by aid of his formula for nitrosopinene, various cases of isomerism which occur in connection with various derivatives of nitrosopinene. The nitrosopinene obtained from the nitrosochloride is different from the nitrosopinene prepared from the former *viâ* pinylamine, pinocarveol, pinocarvone. Likewise, the amine formed on reduction of the oxime is not identical with pinylamine. In order to explain these differences in the oximes and amines, Wallach had suggested that when nitrous acid acts on pinylamine a migration of the endocyclic double linking into the semicyclic position takes place. Ruzicka and Trebler proved now that on ozonisation nitrosopinene yields an ozonide which on splitting up is transformed into formaldehyde (or formic acid) and *iso*nitrosonopinone (II, semicarbazone, m. p. 220°). From the ozonide of acetylpinylamine there results, by the same treatment, the acetyl derivative of α-aminonopinone, m. p. 120 to 121°. It follows from these reactions that in nitrosopinene (III) and pinylamine the double bond is in semicyclic position and that both bodies are derivatives of β-pinene. This new formula for nitrosopinene is in accord with Bredt's rule according to which camphor derivatives, on stereochemical grounds, are non-capable of existance, whenever a double bond proceeds from a carbon atom which is in common with two rings.

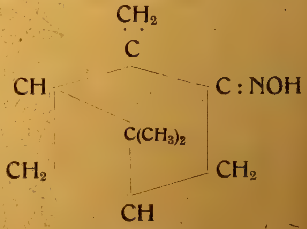
Since pinene nitrosochloride is optically inactive, the two oximes, in the opinion of the authors, must be geometrical isomerides.



(I) Nitrosopinene (Old, incorrect formula).



(II) *Iso*nitrosonopinone.



(III) Nitrosopinene.

As to the preparation of *pinene nitrosochloride*, see p. 137 of this *Report*.

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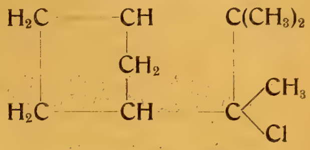
[1]) Cf. *Bericht* (Germ. ed.) 1921, 106. — [2]) *Helvet. chim. acta*, 4 (1921), 566. — [3]) *Liebig's Annalen* 389 (1912), 185.

Camphene.—The body m. p. 157° known generally in literature as camphene hydrochloride resulting from the treatment of camphene with an excess of gaseous hydrogen chloride should be termed appropriately iso*bornyl chloride*, as we learn from a patent application by the firm of Schering[1]), since it is a stereoisomeride of pinene hydrochloride, or bornyl chloride. The true *camphene hydrochloride* (hitherto unknown), *i. e.*, the primary addition product of hydrogen chloride to camphene, is easily obtained by the action of hydrogen chloride on a solution of camphene, when care is taken to avoid any excess of the acid.



Camphene hydrochloride.

Camphene hydrochloride occurs in snow-white crystals (m. p. 125 to 127°) and shows a strong odour of menthol differing enterely from that of pinene hydrochloride or *iso*bornyl chloride. The compound splits off HCl soon after its preparation, and readily passes over into *iso*bornyl chloride, so it is stable only for a short time. Camphene hydrochloride, on shaking with water, or preferably on treatment with alkalies, is transformed nearly quantitatively into camphene hydrate.

J. Schindelmeiser[2]) reports on attempts to split off hydrogen chloride from pinene monohydrochloride by means of Reychler's reaction (with potassium phenate) with the object of obtaining camphene and camphor. Anhydrous potassium phenate (2 mol.) prepared with an excess of potassium hydroxide was mixed thoroughly with pinene hydrochloride (1 mol.) and the mixture distilled immediately. After removing the phenols the author was able to prove, in the distillate, the presence of camphene (in shape of *iso*bornyl acetate after heating with glacial acetic acid in a sealed tube; *iso*borneol, m. p. 212°; from the latter, camphene, m. p. 50°, $\alpha_D \pm 0$) and of bornylene, besides some terpinene and diphenyl oxide (m. p. 28°, b. p. 246°). Since, however, this process allows but 25 per cent. of the pinene to be transformed into camphor, it is of no interest from a commercial standpoint. The oil of *Abies sibirica*, Ledeb. offers a more advantageous crude material, as it contains 35 to 50 per cent. of bornyl acetate. Schindelmeiser was able to split off the acetic acid readily and quantitatively by a very cheap process; the borneol obtained was successfully transformed into camphor on commercial scale by electrical processes. A Franco-Japanese company intends, as per Schindelmeiser, to obtain camphor on a large scale in Siberia from the oil of the Siberian pine.

On α- and β-pinene, from French turpentine oil, compare p. 74 of this *Report*.

Limonene.—A process for obtaining limonene and pinene nitrosochlorides, worked out years ago by K. Löffl[3]), is published by H. Rupe[4]). It gives far better yields than the usual method (with ethyl or amyl nitrite) and consists in introducing a mixture of nitrous gases and hydrogen chloride into a solution of the hydrocarbon. The gases must be mixed in the correct proportion and must react at a temperature as low as possible. If hydrogen chloride is in excess only a green oil results with but very little crystalline nitrosochloride, the amount of which otherwise reaches 90 per cent. of that calculated[5]).

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[1]) Germ. pat. appl. C. 29517, Sept. 25, 1921. — [2]) *Pharmacia* **1921**, N° 1 (Reval). As per a copy kindly forwarded to us. — [3]) *Über Reduktionen in der Reihe der cyclischen Oxime und Nitrosochloride.* Dissertation, Basle **1915**. — [4]) *Helvet. chim. acta* 4 (1921), 149. — [5]) According to Wallach (*Terpene und Campher*, 2nd ed., p. 69) the preparation of nitrosochlorides by Tilden's process (introducing vapours of nitroxyl chloride into the chloroform solution of the terpenes at —10°) is troublesome. Wallach's method (treatment with amyl nitrite and concentrated hydrochloric acid), however, works quickly and satisfactorily.

The investigation of the *sesquiterpenes* by means of the usual oxidation processes, or with application of heat, has hitherto not been very satisfactory. L. Ruzicka and J. Meyer[1]) undertook to elucidate the constitution of these bodies by aid of the dehydrogenation method. For this reason, the author heated cadinene (b. p. 134 to 136° at 13 mm.) with sulphur to 200 to 265°. After repeated distillation with sodium they arrived at a naphthalene hydrocarbon $C_{15}H_{18}$ (b. p. 157 to 158° at 12 mm.; 291 to 292° at 720 mm.; $d_{4^{\circ}}^{19^{\circ}}$ 0.9792; $n_{D19^{\circ}}$ 1.5851; mol. refr. $C_{15}H_{18}/\overline{\overline{5}}$ calc. 64.73, found 67.78) which was transformed into the picrate $C_{21}H_{21}O_7N_3$ (m. p. 115°) and regenerated from the latter, hence was obtained in the pure state.

The hydrocarbon behaved like a fully saturated body when treated with a solution of bromine in carbon disulphide, or of potassium permanganate. On mixing with an alcoholic solution of trinitroresorcinol the hydrocarbon yielded the styphnate $C_{21}H_{21}O_8N_3$, m. p. 138°. By reduction with sodium and ethyl alcohol the authors obtained the dihydro compound $C_{15}H_{20}$ (b. p. 151 to 153° at 12 mm.) which was oxidised already by dilute permanganate solution with formation of acids and which gave no addition-product with picric acid.

The authors obtained likewise from a fraction b. p. 125 to 138° (12 mm.) containing cadinene from East Africa copaiba balsam oil by treatment with sulphur products yielding the identical picrate of the m. p. 115°. Hence other sesquiterpenes occuring in East African copaiba oil, provided they are derivatives of naphthalene, must contain the same nucleus as does cadinene.

On *tetrahydroatractylene*, vide p. 48 of this *Report.*

Concerning *machilene*, see p. 48 of this *Report.*

Alcohols.

A process invented by C. Paal[2]) for the preparation of inactive *citronellol* (dihydrogeraniol) by reducing geraniol with hydrogen in presence of palladium or platinum has been patented in Switzerland[3]).

G. Vavon and J. Detrie[4]) publish various details on the preparation of cyclo*hexanol* by hydrogenating phenol. The yield of *cyclo*hexanol differs but slightly (about two-thirds of the phenol used) even if the details of the process are varied widely. The velocity of the reaction is great; 400 g. of phenol, dissolved in 300 g. of acetic acid, added by aid of 15 g. platinum up to 100 litres of hydrogen per hour. Hydrogenation proceeded far less smoothly when the hydroxyl group was absent, or when it was linked to an alcoholic or acid radical. *Cyclo*hexanone was proved to appear as intermediate product and disappears again, as the reaction passes on.

Terpineol. — By heating terpin hydrate with an organic sulphonic acid, preferably with quinoline sulphonic acid, R. Marchand[5]) obtained terpineol.

On condensing citronellal with acetic anhydride R. H. Pickard, H. Hunter, W. Lewcock and H. Smith de Pennington[6]) obtained only two (and probably no more) of the four possible isomerides of iso*pulegol,* these two being *l-* and *d-α-iso*pulegol. As the yield

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[1]) *Helvet. chim. acta* 4 (1921), 505. — [2]) Cf. Germ. Pat. 298193, Aug. 7, 1913. — [3]) Swiss Pat. 89555, Dec. 17, 1919. As per *Chem. Zentralbl.* 1921, IV. 1323. — [4]) *Compt. rend.* 172 (1921), 1231. — [5]) Brit. Pat. 153605, Dec. 9, 1920. As per *Chem. Zentralbl.* 1921, II. 359. See also p. 141 of this *Report.* — [6]) *Journ. chem. Soc.* 117 (1920), 1248.

of the *iso*pulegyl acetates rarely amounted to 50 per cent., it was probable that the aldehyde taking part in the condensation is the pure dextrorotatory compound of the formula $CH_2 : C(CH_3) \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CHO$1).

The hydrogen phthalate of the mixture of alcohols obtained from the condensation product could be separated by the fractional crystallisation of the magnesium and strychnine salts. Magnesium l-*iso*pulegyl phthalate, $C_{35}H_{42}O_8Mg \cdot 6H_2O$, m. p. 111°; strychnine salt, m. p. 205°; l-*iso*pulegol, b. p. 88° (10 mm.); d-α-*iso*pulegol (still containing, apparently, about 10 per cent. of l-*iso*pulegol), $d\frac{19.5°}{4°}$ 0.9172; $[\alpha]_{D 19.5°} + 29.3°$. On oxidation with chromic acid at 50°, gave *iso*pulegones which gave identical lævorotatory oximes (m. p. 121°, volatile in steam) and semicarbazones (m. p. 171°. When reduced by hydrogen, the alcohols formed *l*- and α-*neo*menthol respectirely, both of which, when oxidised, gave *l*-menthone.

The authors then give extensive tables on the constants of l-*iso*pulegol and its esters with the fatty acids (C_2 to C_{14}) and graphs on the rotation of the esters as influenced by temperature and wave-length.

Menthol. — In a paper entitled, "Contributions towards the knowledge of derivatives of *l*-menthol" *(Zur Kenntnis der Ableitungsprodukte von l-Menthol),* E. A. Lück2) reports on some preparations obtained by him from *l*-menthol and menthone. By heating of menthol with concentrated sulphuric acid for one hour he claims to have obtained a sesquiterpene $C_{15}H_{24}$ or $C_{30}H_{48}$ *(sic)* brownish-black, thickish mass) and furtheron, by nitration, a nitrososesquiterpene (! nitrosesquiterpene) $C_{30}H_{47}NO_2$ (decrepitating on heating). Lück prepared also a menthyl cyanide and herefrom a menthane carboxylic acid (termed by him methylene mentholic acid [*sic*]; white needles, the m. p. of which could not be kept constant [*sic*]), the corresponding aldehyde, and from the latter the secondary (!) alcohol, and a ketone.

All these bodies are enumerated with their constitutional formulæ (as Lück imagines them to be) but without the least proofs of identity, without giving the necessary constants, or any analytical results. It is desirable that the autor may supplement his work in this respect and thus elucidate its results.

Borneol. — A process has been published3) for the preparation of borneol from turpentine oil, consisting in treating the oil with tetrachlorophthalic acid and decomposing the resulting dibornyl ester of the acid with alcoholic caustic soda solution. A mixture of one pt. tetrachlorophthalic acid and 4 pts. turpentine oil, or crude pinene is heated for twelve hours to 106 to 108°, then for two hours to 125°, and finally for six hours to 140°. After cooling the unattacked terpenes are removed by steam or vacuum-distillation and the residue, mainly dibornyl tetrachlorophthalate, is saponified by alcoholic sodium hydroxide. The borneol, purified in the usual manner, is optically active and free from *iso*borneol. The yield amounts to 17 to 18 per cent. of the crude pinene employed. A large portion of the pinene as well as the tetrachlorophthalic acid is recovered.

If an organic solvent, such as anisole, a ketone, or an aromatic ester, is added to the mixture of pinene and acid prior to the heating, the reaction passes off more smoothly and the yield is raised up to 29 per cent.4).

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1) Cf. the paper by Prins, *Chem. Weekbl.* **14** (1917), 692; *Report* **1918**, 123. — 2) *Apotheker-Ztg.* **36** (1921), 279. — 3) *Fabriques des produits chimiques de Thann et de Mulhouse.* Fr. Pat. 510002, Nov. 25, **1920**. Brit. Pat. 144604, Dec. 3, **1919**. Germ. Pat. Appl. F. 47011 published Jan. 12, **1922**. — 4) Brit. Pat. 158533, Nov. 1, **1920**. (Add. Pat. to Brit. Pat. 144604.) As per *Journ. Soc. chem. Industry* **40** (1921), A. 561.

According to another process devised by L. Schmidt¹) the bornyl and *iso*bornyl esters of organic acids are obtained in a good yield and free from by-products when these acids are heated with pinene or pinene-containing oils with an addition of boron trioxide. This latter reagent acts as a general condensing agent for pinene and organic acids by which pinene is esterified in a short time quantitatively even in open vessels. It is said to offer particular advantage to act on the mixture with boric, metaboric, or tetraboric acids on the anhydrides of the organic acids. For instance, 13.6 pts. of pinene or turpentine oil, 9 pts. of glacial acetic acid, and 1 pt. of boron trioxide are heated to its the boiling point under a reflux tube, until the ester content increases no more. The ester mixture is washed with water and fractionated *in vacuo* and yields on saponification with alcoholic potash pure borneol + *iso*borneol with a m. p. of 197 to 199°. The unchanged boron trioxide can be used again.

The process may be modified²) by substituting the boron trioxide by so-called mixed anhydrides of boric and of organic acids, such as boric acetic anhydride. This mixed anhydride, a simple additional product of the formula:—

$$3\,\begin{matrix}R-CO\\R-CO\end{matrix}\!\!>O + B_2O_3 = 2B(O\cdot CO\cdot R)_3$$

is preferably prepared in the course of the reaction. For instance, 136 kg. of pinene, 60 kg. of glacial acetic acid, 10.2 kg. of acetic anhydride, and 2.3 kg. of boron trioxide are heated together for several hours on a water-bath, the reaction-product is rinsed with water as soon as the ester-content has reached a maximum, and the acetates of borneol and *iso*borneol are obtained by fractional distillation. Saponification yields a mixture of pure borneol and *iso*borneol, m. p. 197 to 198°.

F. Martin³) started some experiments on the acetylation of borneol and *iso*borneol. His investigation culminated in the result that in estimating borneol or alkylborneol the alcohol must be heated for three hours with 3 parts of acetic anhydride and some sodium acetate up to 145 to 150°. With less time, or less acetic anhydride, acetylation remains incomplete, as Martin states. (The acetylation was performed in an oil bath at a temperature close to the boiling point.)

Contrary to these statements it is quite sufficient when in the quantitative acetylation of borneol, equally so of geraniol, menthol, and santalol, 10 ccm. each of the alcohol and of acetic anhydride are boiled for one hour with 2 g. of sodium acetate. Years ago⁴) we established, by way of experiment, the correctness and practicability of this method.

According to L. G. Wesson⁵), iso*bornyl ester* and *camphene* are obtained by heating a mixture of a carboxylic acid and of pinene hydrohalide with some zinc, the proportion of which not exceeding 5 per cent. of the pinene hydrogen halide employed.

Carvomenthol.—When reducing α-phellandrene nitrite with sodium and alcohol, Wallach and Herbig⁶) had obtained, in addition to tetrahydrocarvone (carvomenthone) and tetrahydrocarvylamine, *l*-tetrahydrocarveol (*l*-carvomenthol), but they abstained from examing the resulting alcohol for optical isomerism. V. Paolini⁷), on repeating these experiments, found that two isomeric forms of *l*-carvomenthol are generated in the

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¹) Germ. Pat. Appl. Sch. 50927, Oct. 3, **1921**. — ²) Germ. Pat. Appl. Sch. 53704, Oct. 3, **1921**. Add. to Appl. Sch. 50927. — ³) *Journ. de Pharm. et Chim.* VII. **23** (1921), 168. — ⁴) *Report* April **1910**, 155. — ⁵) U. S. Pat. 1372382, March 22, **1921**. As per *Chem. Zentralbl.* **1921**, II. 1063. — ⁶) *Liebig's Annalen* 287 (1895), 378. — ⁷) *Rend. della R. Accad. dei Lincei* **30** (1921), 265. As per a separate copy kindly forwarded to us.

process. The tetrahydrocarveol obtained from nitro-α-phellandrene (α-phellandrene, b. p. 75° at 15 mm.; d_{15° 0.848; α_D —81° 30′; n_{D20° 1.4769) by reduction with sodium and absolute alcohol showed the following constants:—b. p. 218° (corr.); d_{15° 0.9073; $[\alpha]_D$ —10.83°, n_{D15° 1.463. From this alcohol the author prepared, by the cold process, the hydrogen phthalate of *l*-carvomenthol (m. p. 89°; $[\alpha]_D$ —45° 4′) which yielded on saponification pure *l*-α-carvomenthol (b. p. 218° [corr.]; d_{15° 0.9074; α_D —20.38°; n_{D15° 1.463). From the mother liquor of the carvomenthol phthalate mentioned above a second, syrupy hydrogen carvomenthol phthalate was produced, which on transformation into its silver salt (m. p. 175 to 176°) yielded furtheron *l*-β-carvomenthol (b. p. 218° [corr.]; d_{15° 0.9071; $[\alpha]_D$ —8.63°; n_{D15° 1.463). Paolini proposes to term the isomeric carvomenthols obtained by him[1]) from carvone, for sake of differentiation, *d*-γ-carvomenthol ($[\alpha]_D$ +1.82°) and *l*-γ-carvomenthol ($[\alpha]_D$ —1.83°).

Furthermore, Paolini[2]) succeeded in obtaining from *d*-carvone, by following the directions given by Vavon[3]), on reduction with hydrogen and platinum, a carvomenthol, the constants of which were in accord with those of Vavon's preparation, with exception of the rotation ($[\alpha]_D$ —2.75°, instead $[\alpha]_D$ —24.7°). Paolini proved the products with different rotatory power to consist of mixtures of optical isomerides. Either the one or the other isomeride preponderated, according to the more or less complete process of the reduction. From carvomenthol ($[\alpha]_D$ —2.75°) the author, by aid of his so-called cold process[1]) (*viâ* the di-*d*,β-carvomenthyl phthalate, m. p. 85°, $[\alpha]_D$ +38.53°), was able to separate two isomeric compounds:—*d*,β-carvomenthol (b. p. 218° [corr.]; d_{15° 0.9074; $[\alpha]$ +8.29°) and *l*,β-carvomenthol (b. p. 218° [corr.]; d_{15° 0.9073; $[\alpha]_D$ —8.54°; n_{D15° 1.463; identical with the one of the two isomerides resulting from nitrophellandrene, see above).

Terpin hydrate.—According to a patent granted to the *Société Landaise du terpinéol*[4]), terpin hydrate may be obtained from turpentine oil by means of the following contrivance:—A wooden vat, lined with lead, and filled with turpentine oil and dilute acid, is connected with two pumps of acid-resisting metal. The suction pipe of the one pump dips into the acid, that of the other into the oil, whereas the discharge pipes terminate in the oil and the acid respectively. On putting both pumps in motion a very close mixture of both acid and oil results within a short time, yielding terpin hydrate.

Terpin hydrate is, according to R. Marchand[5]), obtained in almost theoretical quantity and in the crystalline state on mixing oil of turpentine (one pt.) with a 23 per cent. sulphuric acid (2 pts.) and shaking vigorously in an atmosphere of nitrogen or carbon dioxide for about 90 hours.

Concerning the estimation of terpin hydrate, see p. 113 of this *Report*.

P. Lipp and C. Padberg[6]), with the object of studying the behaviour of apo*tricyclol* (I), a derivative of the hitherto unobtainable *cyclo*propanol (II), prepared the first-mentioned alcohol from tricyclenic acid amide (III), which, owing to the lability of the trimethylene ring was primarily degradated according to Hofmann-Jeffreys[7]) down to *apo*tricyclylmethylurethane (m. p. 114 to 116°). In this reaction, tricycloyl-*apo*tricycyl-urea (decomp.

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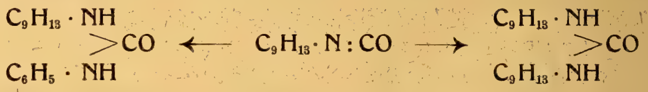
[1]) Cf. *Bericht* (Germ. ed.) **1921**, 113. — [2]) *Rend. della R. Accademia dei Lincei* **30** (1921), 371. As per a reprint kindly forwarded to us. — [3]) Cf. *Report* October **1911**, 150. — [4]) Fr. Pat. 522657, Aug. 14, **1920**. See also *Chem. Zentralbl.* **1921**, IV. 1328. — [5]) Brit. Pat. 153606, Nov. 10, **1920**. As per *Journ. Soc. chem. Industry* **40** (1921), A. 716. — [6]) *Berl. Berichte* **54** (1921), 1316. — [7]) *Berl. Berichte* **30** (1897), 898.

p. 238 to 239° [corr.], on slow heating) resulted as by-product, the *iso*cyanate formed in the main reaction acting with some of the unattacked amide:—

$$C_9H_{13}N:C:O + H_2N\cdot CO\cdot C_9H_{13} = C_9H_{13}\cdot NH\cdot CO\cdot NH\cdot CO\cdot C_9H_{13}.$$

Careful saponification, performed by fusing with solid caustic potash, yielded *apo*tricyclylamine $C_9H_{13}NH_2$, m. p. 104° (unsharp), besides camphenilone and camphenilol.

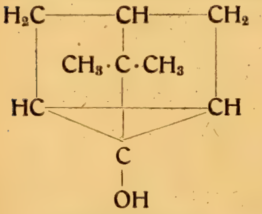
With the object to characterise the unstable *apo*tricylylamine, the authors brought the body in reaction with, *inter alia,* phosgene, obtaining thereby as primary reaction-product a liquid compound, probably *apo*tricyclyl *iso*cyanate. The latter was transformed by aniline into *apo*tricyclyl-phenyl-urea, partly also into symm. di-*apo*tricyclyl-urea:—



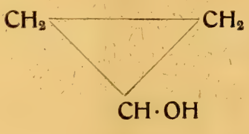
$$\begin{matrix} C_9H_{13}\cdot NH \\ C_6H_5\cdot NH \end{matrix}\!\!>CO \longleftarrow C_9H_{13}\cdot N:CO \longrightarrow \begin{matrix} C_9H_{13}\cdot NH \\ C_9H_{13}\cdot NH \end{matrix}\!\!>CO$$

*Apo*tricyclylphenylurea. *Apo*tricyclyl *iso*cyanate. Di-*apo*tricyclylurea.

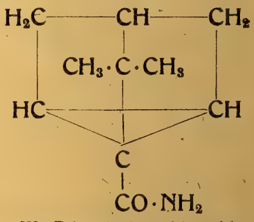
On diazotising the hydrochloride of *apo*tricyclylamine with sodium nitrite, *apo*tricyclol resulted, the reaction passing off fairly well; intermediarily, a comparatively stable nitrite was formed. The alcohol *apo*tricyclol (m. p. 75 to 80° [unsharp], b. p. 82 to 86° at 12.5 mm.; phenylurethane, m. p. 121.6 to 122° [corr.]), on exposure to the air, deliquesces in the course of a few hours forming a viscid oil. When boiled with a dilute mineral acid, equally when heated (without water, by ketisation) in a current of dry hydrogen, *apo*tricyclol yields quantitatively camphenilone. With phosphorus pentachloride, *apo*tricyclol passes over into camphenilone dichloride (IV), m. p. 168 to 169°. Ethereal solutions of the alcohol, on treatment with metallic sodium, yielded, without evolution of hydrogen, the sodium compound of camphenilone pinakone (V) from which the methyl ether was obtained, dimethyl sulphate reacting quantitatively, and methyl iodide only partly.



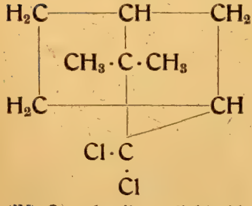
(I) *Apo*tricyclol.



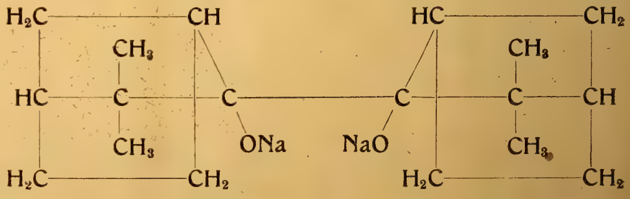
(II) *Cyclo*propanol.



(III) Tricyclenic acid amide.



(IV) Camphenilone dichloride.



(V) Sodium compound of camphenilone pinacone.

As to optical investigations of *geraniol* and *citronellol,* vide p. 116 of this *Report.*

The publications by Fromm and Klein on *olibanol* (see p. 36 of this *Report*) and by Müller on the constitution of *reuniol* (see p. 116 of this *Report*) are discussed by H. Heller[1].

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[1] *Deutsche Parf.-Ztg.* 7 (1921), 22.

On a new *α,β-ketonic alcohol* $C_9H_{10}O_2$, compare p. 150 of this *Report.*

From atractylol, Seisi Takagi[1] obtained, by reduction with hydrogen and platinum in glacial acetic acid, *dihydroatractylol* $C_{15}H_{28}O$ as a viscid oil, $[\alpha]_{D12^\circ} + 14.9^\circ$.

Aldehydes.

K. W. Rosenmund and F. Zetsche[2], by catalytic dehydrogenation by means of the "copper-quinoline-nitro-body" and of oxygen, obtained from primary aliphatic, aromatic and equally hydrocyclic alcohols the *aldehydes,* from secondary alcohols the *ketones.* Tertiary alcohols remain unaffected. The following examples are cited by the authors:— benzophenone from benzhydrol (yield, 92 per cent.), "fermentation" valeric aldehyde from "fermentation" amyl alcohol (80 per cent.), acetaldehyde from ethyl alcohol (52 per cent.), propionic aldehyde from propyl alcohol (5 per cent.), *iso*butyric aldehyde from *iso*butyl alcohol (75 per cent.), *o*-chlorobenzaldehyde from *o*-chlorobenzyl alcohol (86.2 per cent.), fural from furyl alcohol (74 per cent.). The method is particularly suited with the difficultly, or non-volatile, alcohols; with the volatile alcohols, the method offers no advantages compared with the usual processes.

The method worked out by Rosenmund and Zetsche[3] for the catalytic preparation of aldehydes from the corresponding acid chlorides lends itself likewise to the preparation of polyaldehydes, as the authors found in community with Chr. Flütsch[4]. The following aldehydes were obtained by this method, with an average yield of 75 to 85 per cent.:—octanedial = suberic dialdehyde (di-semicarbazone, m. p. 183 to 185°; dioxime m. p. 152°); phen-dimethylal-1,3 = *iso*phthalic dialdehyde, m. p. 88 to 89°; phen-dimethylal-1,4 = *tere*phthalic dialdehyde, m. p. 116°. *Ortho*phthalic dialdehyde, however, was unobtainable from the *o*-phthalic acid chloride, probably the *o*-acid dichlorides are rearranged to the asymmetric form owing to the palladium chloride formed in the reduction.

The following process for preparing *aromatic hydroxyaldehydes* has been patented in the U. K. in favour of the Société chimique des usines du Rhône[5]:—Phenols or their derivatives are treated at suitable temperatures with formaldehyde in presence of a nitroso compound, such as nitrosobenzene, nitrosonaphthalene, or *p*-nitrosodimethylaniline. If necessary, a condensating agent, *e. g.,* hydrochloric acid, is added. When the reaction has passed off the solvent is removed by distillation and the hydroxy aldehyde worked up as usual.

The specification deals with the preparation of vanillin by starting from guajacol, formaldehyde, and *p*-nitrosodimethylaniline. In the same manner anisic, protocatechuic, *p*-hydroxybenzoic, and salicylic aldehydes are obtainable.

Closely related to this process is the method specified by H. Haakh[6]:—Phenols, or derivatives thereof, are allowed to react with formaldehyde, or bodies splitting off formaldehyde, and aromatic nitroso compounds, *e. g.,* *p*-nitrosodimethyl(ethyl)aniline, *p*-nitrosophenol, in presence of a condensing medium (hydrochloric acid). By this method, anisic aldehyde may be prepared from anisole, and vanillin from guajacol.

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[1] *Journ. pharm. Soc. Japan* **1921,** N° 473. Cf. also p. 47 of this *Report.* — [2] *Berl. Berichte* **54** (1921), 2033. — [3] Cf. *Report* **1918,** 122. — [4] *Berl. Berichte* **54** (1921), 2888. — [5] Brit. Pat. 161679, April 13, **1921**; cf. also French Pat. 523407, Aug. 18, **1921,** and Swiss Pat. 95560, Nov. 1. **1921.** — [6] Brit. Pat. 157850, Febr. 17, **1921.** As per *Chem. Zentralbl.* **1921,** IV. 121.

Polymerisation of the most unstable acrolein to insoluble disacryl may be prevented, as was found by Ch. Moureu, Ch. Dufraisse, P. Robin, and J. Pougnet1), by adding a small amount of phenols or bodies containing such, such as pyrogallol (in proportion 1 : 1000), pyrocatechol or hydroquinone (1 : 500), gallic acid (1 : 250), or ethereal tannin solution (1 : 100). Extracts of tanning agents act in the same manner. These phenols are likewise capable of arresting the once started polymerisation of acrolein. The aldehyde, when treated wifh these agents, remains stable for years, provided that it is kept in the dark and at a temperature not exceeding 30°.

Citral. — E. Knoevenagel and G. Oelbermann2) have continued the work of the first-named author3) on testing the constitution of compounds of the citral series by optical methods. The values observed by the authors of the specific normal exaltation of citral were in good accord with the figures observed formerly by v. Auwers and Eisenlohr, as well as with those found by the last-named investigator for the system —C(R):CH·CHO ($E\Sigma_{Refr.}$ 1.25; $E\Sigma_{Disp.}$ 45 per cent.). Whereas a preparation of citral after keeping for 48 hours at a temperature of —190° had suffered a slight change (the refractive index rising from 1.48786 to 1.48821), another preparation remained unchanged after the same treatment. After three months' standing in the same sealed bottles, the preparation, on optical examination, showed a strong increase in density and a decrease in the molecular refraction. Possibly, it was the case of polymerisation, or oxidation, or of both.

With *pseudo*ionone, the authors obtained values equally in good accord with those recorded by Eisenlohr for the system —C(R):CH·CH:CH·C(R):O ($E\Sigma_{Refr.}$ somewhat above 2.7; $E\Sigma_{Disp.}$ above 110 per cent.). The optical constants remained unchanged after cooling the preparation down to —190° for 300 hours.

From *pseudo*ionone, *ψ-ionone acetate* was prepared according to Knoevenagel, by means of acetic anhydride with addition of sublimed ferric chloride. B. p. 145 to 146° (15 mm.). Basing on the values read off for the exaltations ($E\Sigma_{Refr.}$ +0.29 and +0.42; $E\Sigma_{Disp.}$ +7 and +8 per cent.) the authors suggest formula (I) for the acetate, although they admit that various isomerides may be present. This assumption is rendered probable by the wide b. p. range of the freshly-prepared acetate, the main part of which boiled from 118 to 150° at 11 mm. No alteration of the optical values was noticed after cooling down to —190° during 300 hours.

For *iso-ψ*-ionone, obtained from the preceding acetate by boiling with alcoholic caustic potash (b. p. 128 to 129° at 13 mm.) the author suggest formula (II) in view of the exaltations found ($E\Sigma_{Refr.}$ +2.22 and +0.39; $E\Sigma_{Disp.}$ +10 and +14 per cent.). Cooling down to —190°, for 300 hours, did not affect the body; however, after ten hours' standing in an open vessel the molecular refraction, by oxidation, rose from 1.49805 to 1.50311, and after 17 hours to 1.50350. The semicarbazone, m. p. 189°, was identical with a semicarbazone obtained in the same manner from ψ-ionone acetate.

By abstracting water from ψ-ionone with zinc chloride, the authors obtained two fractions of a hydrocarbon (not quite pure, b. p. 90 to 122° [12 mm.] and 135 to 145° [21 mm.]), concerning the constitution of which nothing certain could be stated from the optical data or the chemical reactions (preparation of an oxidation-product).

The optical dispersion observed with α-citrylidene acetoacetic ester was somewhat too low, since that body is easily rearranged into the β-isomeride and therefore

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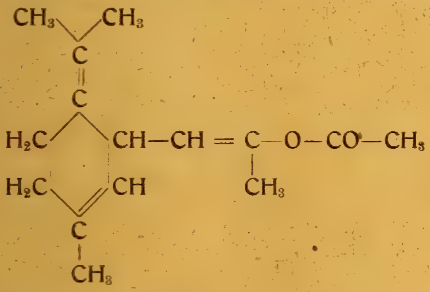
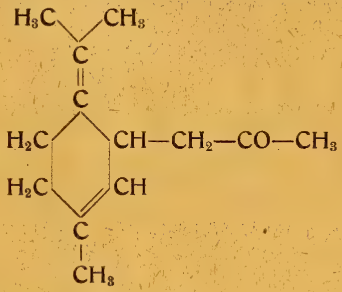
1) Process for stabilising acrolein. Germ. Pat. Appl. M/64903, April 7, 1921. — 2) *Journ. f. prakt. Chem.* N. F. 102 (1921), 305. — 3) Cf. *Report* 1919, 147.

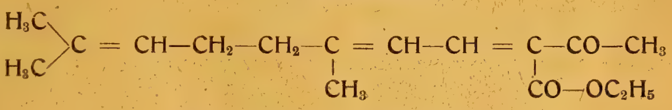
is difficultly obtainable in the pure state. In view of this circumstance and of the optical constants found by them the authors regard the formula (III) of the ester¹), as suggested by Steinle, as the correct one.

From a citrylidene acetoacetic ester the authors prepared, *viâ* the *α-iso*ester, *α-iso*-ionone. In order to make the methods of preparation agree with the optical data, Knoevenagel and Oelbermann assign to this ketone formula (IV) in lieu of formula (II) hitherto accepted which they suggest for *iso-ψ*-ionone.

When examining *β*-citrylidene acetoacetic ester, the optical constants were not found to agree with the formula propagated by Mechtersheimer²) which constitutes a simple, "disturbed" conjugated system. The optical data would agree best with formula (V), with cumulated double bonds, the presence of which, however, has not been proved hitherto.

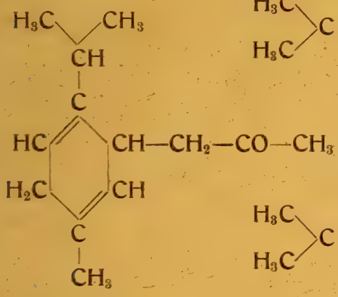

(I) *Pseudo*ionone acetate.

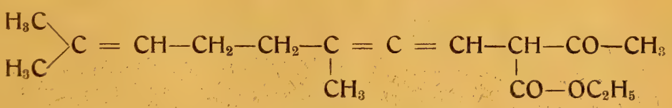

(II) Iso*pseudo*ionone.



$$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>C=CH-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH=\underset{\displaystyle CO-OC_2H_5}{\underset{|}{C}}-CO-CH_3$$

(III) *α*-Citrylidene acetoacetic ester.


(IV) *α-Iso*ionone.



$$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>C=CH-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=C=CH-\underset{\displaystyle CO-OC_2H_5}{\underset{|}{CH}}-CO-CH_3$$

(V) *β*-Citrylidene acetoacetic ester.

From the *β*-ester, a hydrocarbon was prepared according to Mechtersheimer by means of zinc chloride, which was oxidised by a mixture of nitric and sulphuric acids. The resulting body, a solid of the m. p. 154°, has not been examined further.

The formulæ for *β-ψ*-ionone, *β-iso*citrylidene acetoacetic ester, and *β-iso*ionone²) put forward by Mechtersheimer agree approximately with the values observed by the authors.

On benzaldehyde, see p. 90 of this *Report*.

Concerning a specially devised flask for the estimation of *phenylacetaldehyde*, cf. p. 114 of this *Report*.

Salicylic aldehyde and acid are obtained, as per an American Patent 1380277, May 31, **1921** of J. M. Weiss and C. R. Downs³), by oxidising *o*-cresol in the vapour phase with a gas containing oxygen in the presence of a metallic oxide as catalyst.

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¹) Cf. *Report* **1919**, 148. — ²) Cf. *Report* **1919**, 149. — ³) *Journ. Soc. chem. Ind.* **40** (1921), A. 561.

Ketones.

As to the preparation of ketones from secondary alcohols, see page 143 of the present *Report.*

In order to supplement earlier investigations[1], P. Sabatier and B. Kubota[2] publish new details on the catalytic reduction of *benzaldehyde* and of *aromatic ketones* by means of copper. The metal required for their experiments was prepared by slow reduction, at 200°, of black tetracupric hydrate. At 350°, benzaldehyde was reduced to benzene, toluene, and carbonic oxide. Contrary to the reduction performed formerly by aid of nickel, the carbonic oxide was not reduced to methane, but remained unchanged.

Acetophenone and ethylphenylketone were reduced catalytically by copper at 350° to ethylbenzene (b. p. 135°) and propylbenzene (b. p. 158°). Under identical conditions, benzoyl propanone was transformed into acetophenone (fairly good amount), some acetic aldehyde, ethyl alcohol, and ethylbenzene. By reducing benzoquinone over copper, at 300°, nearly exclusively hydroquinone, m. p. 169°, resulted, besides some water and phenol.

Carvone. — A. Müller[3] was successful in preparing crystalline benzalcarvone which hitherto has been obtained by the usual condensation reactions merely as an amorphous product[4]. The condensation of carvone with benzaldehyde passed off by means of alcoholic potash lye at a temperature not exceeding $+2$ to $+3°$. The fraction b. p. 170 to 180° (10 mm.) of the reaction-product constituted the raw material for the preparation of two isomeric benzalcarvones, the residue forming the amorphous body described already by Wallach[2]. After several weeks' standing, a crystalline body separated from the viscous benzalcarvone fraction, β-benzalcarvone, m. p. 114 to 115°, $[\alpha]_D - 815°$ ($\alpha - 8.15°$ of a 1 per cent. alcoholic solution in a 100 mm. tube). The residual α-benzalcarvone, b. p. 191 to 193 (10 mm.); $d_{15°}$ 1.041; $[\alpha]_D + 152.30°$, contained still a considerable amount of the β-isomeride. Neither of the isomerides (which showed red-orange and brick-yellow halochromism respectively) yielded an oxime or a semicarbazone. α-Benzalcarvone yielded an addition-product with hydrogen chloride, a dark brown oil which on heating gave off a fair amount of hydrogen chloride. On reduction with sodium both isomerides yielded benzyldihydrocarveol, the phenylurethane of which (m. p. 233 to 234°) was identical with the derivative of benzyldihydrocarveol obtained from benzaldihydrocarvone.

By means of the method founded on the absorption of ultraviolet light the author proved that on the one hand the curves for β-benzalcarvone and benzalmenthone, on the other hand those for α-benzalcarvone and benzaldihydrocarvone were, in the main identical. This behaviour shows that both β-benzalcarvone and benzalmenthone have identical structure, the former being, therefore, β-3-benzalcarvone.

How the α-isomeride is constituted remains still an open question, since benzaldihydrocarvone may exist also in a second form. As compared with carvone ($[\alpha]_D + 59.5°$), the values for $[\alpha]_D$ with α- and β-benzalcarvone ($+152.5°$ and $-815°$) are exceedingly high. Both isomerides demonstrate very satisfactorily that on introducing aromatic radicals into the nucleus, *i. e.*, by accumulating the double linkings, the rotation is markedly increased.

According to M. Matsui and S. Shimizu[5], *menthone* can be reduced electrolytically in sulphuric or hydrochloric acid solution to menthol. The best results are obtained

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[1] Cf. Sabatier, *La catalyse en chimie organique*, 2nd ed., p. 190 to 196. — [2] *Compt. rend.* **172** (1921), 733. — [3] *Berl. Berichte* **54** (1921), 1471. — [4] *Liebig's Annalen* **305** (1899), 274. — [5] *Mem. Coll. Sci. Kyoto* **4** (1920), 245. As per *Journ. Soc. chem. Ind.* **40** (1921), A. 162.

when using an amalgamated tin or lead cathode, the cathode solution constisting of a mixture of 75 per cent. sulphuric acid (40 to 45 cc.) with 94 per cent. alcohol (35 to 40 cc.) at a temperature below 15°. The current used is 6 to 8 ampères per 100 sq. cm. at 11 to 13 volts. The yield of menthol is only 25 per cent., and the product was difficult to purify. An oily by-product is always obtained, which is a more highly reduced body, possibly menthane.

By reducing *thujamenthone* with hydrogen and nickel at 280°, M. Godchot[1] obtained dimethyl-1,2-*iso*propyl-3-*cyclo*pentane, a liquid of terpene-like odour with the constants: b. p. 148 to 149°, d_{15° 0,793, n_{D15° 1.4364. The same body had been prepared years ago by Godchot and F. Taboury[2] from dihydrocamphorone. On treating thujamenthone with magnesium methyl iodide, Godchot obtained a mixture of two isomeric trimethyl-1,2,3-*iso*propyl-4-*cyclo*pentenes which on further reduction with hydrogen and nickel at 180° yielded the same body, trimethyl-1,2,3-*iso*propyl-4-*cyclo*pentane (b. p. 157 to 158°; d_{13° 0.7833; n_{D13° 1.4326), likewise with a terpene-like odour.

Additionally, the author prepared a new bicyclic ketone, dimethyl-2,3-*iso*propyl-4-*cyclo*pentylidene-dimethyl-2,3-*iso*propyl-4-*cyclo*pentanone-1, by condensing thujamenthone by means of calcium hydride[3]. This new product was a light yellow liquid with a camphoraceous odour and the constants: b. p. 182 to 184° (12 mm.); d_{15° 0.9123; n_{D15° 1.4825.

Camphor. — By acting with sodium *iso*amylate on camphor at 140°, in presence of an excess of *iso*amyl alcohol, F. Martin[4] obtained in a good yield, a mixture of alkyl derivatives of camphor and borneol ("camphol"). He then treated the reaction product, dissolved in benzene, with potassium permanganate and obtained *iso*amylcamphor (b. p. 273°; α_{D18° 59.22°[5]) [in alcoholic solution]; semicarbazone, m. p. 188°). By reducing the reaction-product of camphor and sodium *iso*amylate with sodium and absolute alcohol the author arrived at a white greasy body smelling of borneol; b. p. 190° (61 mm.); $d_{4^\circ}^{0^\circ}$ 0.9611; α_D 16.55°[5]) (in alcoholic solution), which consisted of a mixture of stereomeric bodies. On heating, for three hours, at 140° with the equal part of acetic anhydride and some sodium acetate, the body yielded acetyl*iso*amylcamphol (b. p. 169 to 170° [30 mm.]; $d_{4^\circ}^{15^\circ}$ 0.9402; $\alpha_D + 7.42^\circ$ [in alcoholic solution]; phenylurethane of *iso*amylcamphol, m. p. 111°).

H. Rupe and W. Diehl[6] prepared the following derivatives of *hydroxymethylene camphor:* — methylene camphor-phenylhydroxylamine (m. p. 106 to 107°), the methyl ether of this body (m. p. 75 to 76, very sensitive to light; on exposure to sunlight the compounds deliquesces to a brown mass and separates a sublimate of delicate yellow needles, m. p. 196 to 198°, probably camphor quinone, the ethyl ether of methylene camphor-phenylhydroxylamine (m. p. 162 to 164°), the *p*-nitrobenzoate of the same body (m. p. 179.5 to 180°). On reducing methylene camphor-phenylhydroxylamine, anilidomethylene camphor resulted (m. p. 165 to 167°), which was identical with the anilide obtained by Bishop, Claisen, and Sinclair[7] by condensing hydroxymethylene camphor with aniline.

By heating camphor and fural with sodamide in benzene solution, Wolff[8] arrived at *fural camphor,* m. p. 64°, easily soluble in ether, alcohol, and benzene, less soluble

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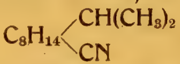
[1] *Compt. rend.* **172** (1921), 686. — [2] *Bull. soc. chim.* IV. **13** (1913), 601. — [3] Cf. *Compt. rend.* **169** (1919), 62. — [4] *Journ. de Pharm. et Chim.* VII. **21** (1921), 417. As per *Bull.* Roure-Bertrand Fils, April **1921**, 104. — [5] The direction of rotation is not given. — [6] *Helvet. chim. acta* **4** (1921), 388. — [7] *Liebig's Annalen* **281** (1894), 358. — [8] *Compt. rend.* **172** (1921), 1357.

in light petroleum. When trying to reduce it to furyl camphor by catalytic reduction according to Sabatier and Senderens in presence of nickel, it was completely reduced to tetrahydrofurylcamphor, b. p. 166° (14 mm.).

Following the process worked out by Haller and Bauer¹) the author prepared, *viâ* the organomagnesium compounds:— phenylfurylcamphor $C_{10}H_{15}O \cdot CH(C_6H_5) \cdot C_4H_3O$, m. p. 114°, benzylfurylcamphor, $C_{10}H_{15}O \cdot CH(C_7H_7) \cdot C_4H_3O$ (viscid oil); *p*-tolylfurylcamphor, $C_{10}H_{15}O \cdot CH(C_6H_4 \cdot CH_3) \cdot C_4H_3O$, b. p. 234° (17 mm.); *p*-anisylfurylcamphor, $C_{10}H_{15}O \cdot CH(C_6H_4 \cdot OCH_3) \cdot C_4H_3O$, b. p. 255° (17 mm.).

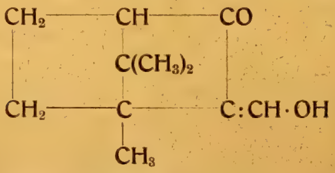
In a later communication, the author publishes the molecular refractions and the specific rotations of the above-mentioned compounds, which agree with the constants found formerly by Haller and Müller²) with the condensation-products from camphor and aldehydes. Furalcamphor shows a strong exaltation of the molecular refraction, the specific rotation, and the molecular dispersion, which is caused by the double bond linked to the furane nucleus and which disappears on reduction.

In connection with earlier work done on mono- and dialkyl derivatives of camphor³), A. Haller and P. Ramart⁴) communicate that the amide of dimethylcampholic acid shows the m. p. 81 to 82° and not, as stated before⁵), 72 to 73°. On reducing this amide with sodium and absolute alcohol, the authors obtained, on rectification, the nitrile of dimethylcampholic acid  $C_8H_{14}\left\langle\begin{matrix}CH(CH_3)_2\\CN\end{matrix}\right.$ (b. p. 131 to 133° [14 mm.], 245 to 247° [ord. press.]). On heating with sulphuric acid to 85 to 100° the nitrile again passes over into the original amide (m. p. 81 to 82°). When the nitrile was reduced with sodium and absolute alcohol, dimethylcampholamine (b. p. 123 to 124° at 20 mm.; $[\alpha]_{D25°} + 30.1°$) resulted in quantitative yield. By reducing the phenyl ester of dimethylcampholic acid (b. p. 190 to 195° at 30 mm.) — not though with the ethyl ester — with sodium and absolute alcohol, the authors obtained dimethylcampholic alcohol (b. p. 139 to 140° at 20 mm.; $[\alpha]_{D24°} + 32°$).

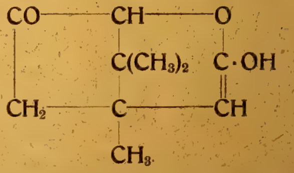
As to the preparation of camphor from pinene hydrochloride see p. 137 of this *Report*.

Epicamphor. — In continuation of the paper by J. Bredt and W. H. Perkin jun.⁶) which dealt with the preparation and the properties of epicamphor, Perkin jun. and A. F. Titley⁷) have prepared some derivatives of *l*-epicamphor which they compare with the analogous bodies obtained from the isomeric *d*-camphor⁸).

When *l*-epicamphor is treated with sodium and *iso*amyl formate in presence of ether, hydroxymethylene-*l*-epicamphor is formed (m. p. 89°, turning but slowly yellow and viscous; semicarbazone, m. p. 197°) to which the authors assign, in analogy to the constitution⁹) assumed for hydroxymethylene-*d*-camphor, the formula (I)



(I) Hydroxymethylene-epicamphor.



(II) Lactone of hydroxyketodihydroepicampholenic acid (tautomeric formula).

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¹) *Compt. rend.* **142** (1906), 971; **146** (1908), 717. — ²) *Ibidem* **128** (1899), 1370. — ³) Cf. *Report* **1919**, 160. — ⁴) *Compt. rend.* **173** (1921), 682. — ⁵) *Report* **1919**, 161. — ⁶) Cf. *Report* April **1914**, 140. — ⁷) *Journ. chem. Soc.* **119** (1921), 1089. — ⁸) *Liebig's Ann.* **281** (1894), 314; **356** (1907), 251. — *Berl. Ber.* **30** (1897), 243. — ⁹) *Journ. chem. Soc.* **95** (1909), 171.

The substance gave a violet coloration when ferric chloride was added to its alcoholic solution, and exhibited mutarotation to a slight extent only, and that in an opposite sense to the mutarotation of the corresponding camphor derivative ($[\alpha]_D$ of a freshly prepared benzenic solution rose from — 125.5° to — 130.5° after 24 hours). Benzoyloxymethylene-epicamphor melted at 106°; aminomethylene-*l*-epicamphor, m. p. 122°, was obtained by heating hydroxymethylene-epicamphor with aqueous ammonia; it does not exhibit mutarotation, contrary to the corresponding camphor derivative. Anilinomethylene-*l*-epicamphor, m. p. 101°, no mutarotation; β-naphthylaminomethylene-*l*-epicamphor, m. p. 109 to 110°, slight mutarotation.

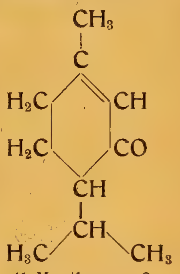
By heating *l*- or *d*-epicamphoroxime with sulphuric acid of 20 per cent. the authors obtained *l*-epicampholenonitrile (b. p. 145° [100 mm.], $[\alpha]_D - 27.4°$, passing over by hydrolysis into *l*-α-epicampholenic acid, b. p. 166° (30 mm.), $[\alpha]_D - 38.4°$ and *d*-epicampholenonitrile (b. p. 146 to 147° [100 mm.], $[\alpha]_D + 26.2°$; *d*-epicampholenic acid, b. p. 164 to 165° [30 mm.], $[\alpha]_D + 39.2°$).

Attempts to prepare β-epicampholenonitrile and its derivatives under the identical conditions as for obtaining β-campholenic derivatives[1]), were unsuccessful.

On reduction, *l*-epicampholenonitril is converted into *l*-epicamphylamine, b. p. 128° (100 mm.).

When *l*-epicampholenic acid is oxidised with potassium permanganate, the main product formed is a mixture of syrupy acids from which a ketonic acid (semicarbazone, m. p. 203°) could be isolated. In addition, there is formed the lactone of hydroxyketodihydroepicampholenic acid (II), m. p. 80°; $[\alpha]_D + 45.8°$. On oxidising the syrupy acids from the permanganate oxidation with chromic acid, an optically active, monobasic acid, (semicarbazone, m. p. 168°) was obtained.

Piperitone. — In their paper on the ketone piperitone contained in various eucalyptus oils, H. G. Smith and A R. Penfold[2]) had arrived at the conclusion that piperitone is either Δ^4-menthenone-3 or Δ^1-menthenone-3. L. Givaudan & Co.[3]) were able to prove that the properties of the ketone — except in its rotatory power — answered to the Δ^1-menthenone-3 prepared originally by Wallach[4]) from a trihydroxyterpane m. p. 120°, subsequently found by us[5]) in Japanese peppermint oil and by Roberts[6]) in the oil of *Cymbopogon sennaarensis*. Hence, Givaudan & Co. regard piperitone as identical with Δ^1-menthenone-3. We wish to add that, although this conclusion does not seem to be fully proved, yet piperitone appears to be a Δ^3-menthenone. The reason for our opinion has been given in our preceding *Bericht* (Germ. ed.) p. 24, footnote.



Δ^1-Menthenone-3.

W. D. Cohen[7]) tested various alcohols as to their power of reducing *benzophenone* when exposed to sun-light. In all cases, whenever a reaction took place, benzopinacone was produced. The presence of water retarded the reaction. The reducing action was: — with methyl alcohol, 100 per cent., *cyclo*hexanol, above 90 per cent., benzyl alcohol about 80 per cent., geraniol about 17 per cent., citronellol and cinnamyl alcohol 0 per cent. of the ketone. The alcohols were transformed respectively into formaldehyde; *cyclo*hexanone; triphenylglycol, resin, a little benzaldehyde; citral.

This reduction of aromatic ketones is a photochemical process and hence the reaction-velocity independent of the concentration of the benzophenone. The oxidation

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[1]) Cf. *Berl. Ber.* **30** (1897), 243, 405. — [2]) Cf. *Bericht* (Germ. ed.) **1921**, 24. — [3]) *Perfum. Record* **12** (1921), 80. — [4]) *Liebig's Annalen* **362** (1908), 271. — [5]) *Report* October **1910**, 97. — [6]) Cf. *Report* **1916**, 18. — [7]) *Rec. trav. chim. Pays-Bas* **39** (1921), 243. As per *Chem. Zentralbl.* **1921**, III. 785.

of the alcohols, however, being a purely chemical reaction depends in its speed on the concentration of the alcohol.

A new optically active α,β-ketonic alcohol $C_9H_{10}O_2$ composed of equal molecules of acetaldehyde and benzaldehyde and possessing the constitution $C_6H_5CO\cdot\overset{*}{C}HOH\cdot CH_3$ or $C_6H_5\overset{*}{C}HOH\cdot COCH_3$ has been obtained by C. Neuberg and J. Hirsch[1]) by means of an enzymatic process. The authors proved with this synthesis, where two aldehydes unite by a fermentation process and form a ketone, that an enzyme exists capable of linking straight-lined carbon chains. This new enzyme connecting carbon with carbon, was termed "carboligase". However, a direct union of acetaldehyde and benzaldehyde by fermentation could not be effected, but it succeeded when the biological predecessor, carboxyacetaldehyde, *i. e.* pyruvic acid, or also sugar, was employed. The authors proceeded in the following manner: — A mixture of sugar, or pyruvic acid, yeast (or the juice of macerated yeast), and benzaldehyde was left to stand for three days and was then filtered and extracted with ether, after the fermentation had come to an end. The residue of the ether was a light yellow oil with a pungent odour reminding of benzyl alcohol (b. p. 102 to 156° at 15 mm.) which gave a strong reaction with sodium nitroprusside and which precipitated instantaneously cuprous oxide from cold Fehling's solution. 0.1 ccm. of the oil dissolved in 10 ccm. of absolute alcohol, showed a rotation of $-0.75°$ in a 100 mm. tube. On standing at the air, signs of decomposition, such as a smell of benzaldehyde, were noticed. The authors were unable to obtain a uniform fraction boiling within narrower limits, in spite of repeated distillation, but they were successful in preparing various derivatives of the product: — phenylhydrazone, m. p. 96°; semicarbazone, m. p. 189°; thiosemicarbazone, m. p. 204 to 205°; *p*-nitrophenylosazone, m. p. 264 to 265° — which served for identifying the product and as a proof for the correctness of the formulæ given above.

It could not be elucidated in which manner the fermentation of sugar or of pyroracemic acid passes off in presence of benzaldehyde. The authors leave it open for discussion whether a specially reactive form of acetaldehyde is formed by the scission of pyroracemic acid with carboxylase, which unites with benzaldehyde, or whether the biological condensation starts already with benzaldehyde and pyroracemic acid.

Phenols and Phenol Ethers.

Carvacrol. — According to Gibbs and Phillips[2]), a good yield of carvacrol is obtained from *p*-cymene sulphonic acid only when the process is carried on in an autoclave. With reference to this statement, A. W. Hixson and R. H. Mc.Kee[3]) claim to have obtained a good yield (76 per cent.) of carvacrol from *p*-cymene sulphonic acid when working at ordinary pressure. The carvacrol of Gibbs and Phillips (prepared with or without pressure) is said to contain 6 to 8 per cent. of thymol, which would escape detection by the method of analysis used by Gibbs and Phillips.

D. C. L. Sherk[4]) has published a thesis entitled, *Thymol and carvacrol problems*, of which we discussed some details in our last *Bericht* (Germ. ed.) **1921**, p. 119. In addition to the compounds mentioned there the author prepared the alkali salts of nitrosocarvacrol and nitrosothymol by dissolving the nitrosophenols in the theoretical

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[1]) *Biochem. Ztschr.* **115** (1921), 282. As per a special copy kindly forwarded to us. — [2]) Cf. *Bericht* (Germ. ed.) **1920**, 147. — [3]) *Journ. ind. eng. Chem.* **12** (1920), 296. — [4]) Thesis (Fritzsche Bros. Fellow), Madison, Wis., **1920**. From a copy kindly forwarded to us.

quantity of 2N-alkali made up free from carbonate, and evaporating to dryness in a vacuum desiccator. The salts were coloured red or blue, corresponding either to the nitroso or to the *iso*nitroso (oximido) type. The silver salt of nitrosocarvacrol was at first greenish-brown, turning later to olive and finally brown.

For identifying both phenols, the benzoyl derivatives of the nitroso compounds are particularly useful:—benzoyl nitrosothymol, (from alcohol, m. p. 109 to 110.5°; no oxime obtainable); benzoyl nitrosocarvacrol (from alcohol, m. p. 85 to 87°; oxime, obtained by treatment with hydroxylamine hydrochloride and sodium bicarbonate; m. p. from benzene, 156 to 157° with evolution of gas). Alkali transforms the oxime into nitroso*thymol.*

By treating the alkali salts of both nitrosophenols with methyl iodide in alcoholic solution, the author obtained nitrosocarvacrol methyl ether (m. p. 39°) and nitrosothymol methyl ether (liquid).

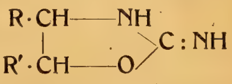
Isosafrole.—S. Nagai[1]) reports on the various geometrical isomerides of *iso*safrole, on which Hoering and Baum[2]) had published a paper some time ago. When safrole is rearranged to *iso*safrole, the stable *trans*-form is obtained best by heating 1 pt. safrole, 0.5 pt. potassium hydroxide, and 1 pt. 98 per cent. alcohol up to 94 to 95° for four to five hours. The labile *cis*-form, which on heating passes over into the other isomeride, is formed when using less alkali and more alcohol and at a lower temperature. The author describes the following preparations:—*c* (*cis*)-*iso*safrole (b. p. 242 to 243°; $d^{15^\circ}_{4^\circ}$ 1.1162 to 1.1168; n_{D15° 1.5630 to 1.5632; picrate, m. p. 68.5°); *t* (*trans*)-*iso*safrole (b p. 247 to 248°; $d^{15^\circ}_{4^\circ}$ 1.1230 to 1.1235; n_{D15° 1.5730 to 1.5736; picrate, m. p. 73.5 to 74°). The dibromides of both isomerides differ merely by the angle of rotation:—*cis*-dibromide, $[\alpha]_{D20^\circ} + 13.35^\circ$, *trans*-dibromide, $[\alpha]_{D20^\circ} + 4.45^\circ$.

By distilling *in vacuo* or by heating with potassium hydroxide, the *t*-dibromide yielded the *c*-monobromide (b. p. 168 [19 mm.]), and *vice versâ,* the *c*-dibromide gave the *t*-monobromide (b. p. 154° [19 mm.]) of *iso*safrole. *cis*-Isosafrole monobromide as well as *t*-dibromide, when heated to 70°, readily split off hydrogen bromide with formation of piperonyl allylene $CH_2O_2 : C_6H_3 \cdot C \vdots C \cdot CH_3$ (m. p. 41 to 42°, b. p. 249 to 251°). On the other hand, *t*-monobromide and *c*-dibromide yielded piperonyl allylene only when heated to 150° and with an excess of alkali.

On heating the monobromides with zinc and alcohol, the author obtained the corresponding *iso*safroles. This reaction furnishes a method of obtaining, from *c*-*iso*safrole, *via* the bromine compounds, *trans*-derivatives, and again leads back to the initial body.

By oxidising both isomerides with potassium permanganate or ozone, the same body, piperonal, resulted.

A new method for the preparation of the *alkamines* of anethole, *iso*safrole, and methyl*iso*eugenol has been published by J. Takeda and S. Kuroda[2]). The *pseudo*-ureas of these bodies, obtained from their dibromides with urea, are constituted, in the opinion of the authors, as demonstrated by the annexed formula, and on treatment with acetic anhydride and sodium acetate they yield the acetyl derivatives and the acetylated oxazolidones. These bodies are broken up, on boiling with alkali, more readily than the ψ-ureas and lend themselves, therefore, preferably for the preparation of the alkamines. Following this method, the authors arrived at the following derivatives:—anethole alkamine



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[1]) *Journ. Coll. Engin.*, Tokyo **11** (1921), 83. From a special reprint kindly forwarded to us. — [2]) *Journ. pharm. Soc. of Japan* **1921**, No. 467. As per *Chem. Zentralbl.* **1921**, I. 789.

$CH_3O\cdot C_6H_4\cdot CH(NH_2)\cdot CH(OH)\cdot CH_3$ (m. p. of the acetyl derivative, 111 to 112°), *iso*safrole alkamine $CH_2O_2 : C_6H_3\cdot CH(NH_2)\cdot CH(OH)\cdot CH_3$ (m. p. 79°), hydrochloride (m. p. 210 to 215°), N-acetyl*iso*safrole alkamine (m. p. 156°), N-benzoyl*iso*safrole alkamine (m. p. 139°), N-dimethyl*iso*safrole alkamine (m. p. 171 to 173°), methyl*iso*eugenol alkamine $(CH_3O)_2 : C_6H_3 : CH(NH_2)\cdot CH(OH)\cdot CH_3$ (m. p. 95 to 96°), hydrochloride (m. p. 222°), N-benzoate (m. p. 140°), N-methylate (m. p. 90 to 91°).

Acids, Esters, and Lactones.

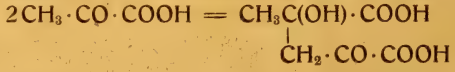
Although the *butyric acid fermentation process* of the carbohydrates has been investigated extensively and has been explained by assuming a condensation process like that of acetaldol, or crotonaldehyde, the experimental ground for this theory was still missing. The process was slucidated only by the investigations of C. Neuberg and his collaborators. Since Neuberg and Nord[1]) had shown that in bacterial degradation in the sugar series, just as in the alcoholic fermentation of sugar by means of yeast, acetaldehyde is formed, Neuberg and B. Arinstein[2]) were now able to perform successfully their investigations on the character of the butyric acid and the butylic alcohol fermentations. Their experiments proved that when starch syrup is fermented by *Bacillus butylicus*, Fitz in presence of calcium carbonate, peptone and a solution of nutrient salts, 25.16 per cent. butyric acid, 7.20 per cent. acetic acid, 1.7 per cent. butylic alcohol, and 2.23 per cent. ethyl alcohol are the result. If under the same conditions di-sodium sulphite is added, with the object to "catch off" and eliminate the intermediarily-formed acetaldehyde, the result runs as follows:—0 per cent. butyric acid, 20.35 per cent. acetic acid, 0 per cent. butylic alcohol, 13.47 per cent. ethyl alcohol, and 7.61 per cent. acetaldehyde; acetic acid and ethyl alcohol may be regarded as dismutation-products of acetaldehyde. These results prove that the formation of acetaldehyde depends in a certain manner on the true saccharogenic butyric fermentation process. The authors found also that α-keto-γ-valerolactone-γ-carboxylic acid, the so-called aldol of pyroracemic acid (see below under b), on fermentation with *Bac. butylicus*, yields butyric acid in addition to some acetic acid. Pyroracemic acid being considered as the intermediary stage of acetaldehyde[3]), it may be assumed that the degradation process of sugar, on butyric fermentation, passes off with pyroracemic acid as intermediate body, this acid being condensed to the aldol and the latter split up to butyric acid.

In the authors' opinion, both processes, that of the butyric acid fermentation and of the butylalcoholic fission of sugar, can be expressed by the following rough formulæ:—

Butyric acid fermentation of sugar:

a) $C_6H_{12}O_6 = 2CH_3\cdot CO\cdot COOH + 4H$

b)



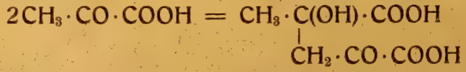
$$2CH_3\cdot CO\cdot COOH = \begin{array}{l} CH_3C(OH)\cdot COOH \\ \quad | \\ \quad CH_2\cdot CO\cdot COOH \end{array}$$

c) $C_6H_8O_6 = 2CO_2 + C_4H_8O_2$.

Butylic alcohol fission of sugar:

a) $C_6H_{12}O_6 = 2CH_3\cdot CO\cdot COOH + 4H$

b)



$$2CH_3\cdot CO\cdot COOH = \begin{array}{l} CH_3\cdot C(OH)\cdot COOH \\ \quad | \\ \quad CH_2\cdot CO\cdot COOH \end{array}$$

c) $C_6H_8O_6 + 4H = 2CO_2 + H_2O + C_4H_{10}O$.

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[1]) *Biochem. Ztschr.* **96** (1919), 133. Cf. *Bericht* (Germ. ed.) **1920**, 140. — [2]) *Biochem. Ztschr.* **117** (1921), 269. As per a special reprint kindly forwarded to us. — [3]) Cf. p. 150 of this *Report*.

Finally the authors were successful in proving a fact of importance from a biological stand-point, that when dextrose is fermented with a pure culture of *Bac. butylicus,* Fitz, caproic acid and higher fatty acids resembling caprylic and caprinic acids are formed.

Of the four *pinononic acids* obtained from different primary bodies, the acid obtained by Kerschbaum on oxidising verbenol from verbena oil was known to be identical with the acid prepared by Blumann and Zeitschel1) from the autoxidation products of pinene (verbenol and verbenone). E. Fromm and R. Klein2) now established the identity of these two acids with the degradation-product obtained by Fromm and Autin3) from olibanol (of frankincense oil). Kerschbaum's pinononic acid semicarbazone (from verbenone), when mixed with the semicarbazone of the acid from olibanol, showed no depression of the melting point. In order to test the behaviour of the fourth specimen of the acid, which had been obtained by Wagner and Ershtchikovski4) by oxidising pinene with permanganate, Fromm and Klein oxidised pure pinene (b. p. 156 to 158°; d_{18° 0.8683), from French turpentine oil, with permanganate according to the directions given. However, instead of the pinononic acid as expected they obtained a pinononic acid contaminated by a small quantity of an acid of the m. p. 100°. They are, therefore, of opinion that the acid obtained by Wagner and Ershtchikovski is due to some impurity in their pinene, preferably to the autoxidation-products containing verbenol and verbenone. For the reason of clearing up this question the authors started some experiments on olibanol, without, however, arriving at the result desired. (Cf. also p. 36 of this *Report.*)

An extensive publication by O. Aschan on *pinabietinic acid,* which we dealt with5) following an abstract from the Swedish, has now appeared in *Liebig's Annalen*6). The crude material serving for the preparation of the acid was a pine oil called in Sweden *Tallolja.* This pine oil results on evaporating the "black lye" *(Schwarzlauge)* of the manufacture of sulphate cellulose and treating the soap obtained therefrom with sulphuric acid or acid sodium sulphate. The product is a dark, thick oil, soluble in sodium carbonate, which by distillation with superheated steam can be separated into readily and difficultly volatile fatty and resinous acids. It was from such a distillate that Aschan obtained pinabietinic acid.

By catalytic hydrogenation with hydrogen in xylene solution, K. W. Rosenmund and F. Heise7) obtained from *benzyl benzoate* and *benzhydryl benzoate* benzoic acid (94 per cent.) and hydrocarbons. If increasing quantities of quinoline were added (0.2 to 1 mgr. to 5 gr. of the ester) the ester saponification was gradually checked. With toluene as solvent the reaction did not take place.

Benzaldehyde, when treated in the same manner in xylene solution, yielded benzyl alcohol (8 per cent.) and preferably dibenzyl ether (52 per cent.). On addition of quinoline in rising quantities, the proportion of the ether formed decreased in favour of the alcohol.

From *benzyl alcohol* and the corresponding acid chlorides H. A. Shonle and P. Q. Row8) prepared the following *esters:* — Benzyl laurate (m. p. 8.5°, b. p. 209 to 211° [11 mm.], $d^{25^\circ}_{25^\circ}$ 0.9457, n_{24° 1.4812), benzyl myristate (m. p. 20.5°, b. p. 229 to 231°

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1) Cf. *Report* October **1913**, 103. — 2) *Liebig's Annalen* **425** (1921), 208. — 3) Cf. *Report* April **1914**, 63. — 4) Cf. *Berl. Berichte* **29** (1896), 881. — 5) Cf. *Bericht* (Germ. ed.) **1920**, 149. — 6) *Liebig's Annalen* **424** (1921), 117. — 7) *Berl. Berichte* **54** (1921), 2038. — 8) *Journ. Americ. chem. Soc.* **43** (1921), 361.

[11 mm.], $d_{25^\circ}^{25^\circ}$ 0,9321, n_{24° 14803), benzyl palmitate (m. p. 36.0°, $d_{25^\circ}^{38^\circ}$ 0.9136, n_{50° 1.4689), benzyl stearate (m. p. 45.8°; $n_{25^\circ}^{50^\circ}$ 0.9075, n_{50° 1.4663), benzyl oleate (liquid at 0°, b. p. 237° [7 mm.], $d_{25^\circ}^{25^\circ}$ 0.9330, n_{25° 1.4875).

For the production of large amounts of these benzyl esters it is recommended to allow benzyl chloride to react with the anhydrous alkali salt of the fatty acid dissolved in an excess of that acid.

From by-products resulting from the hydrolysis of proteins S. Kodama¹) a series of mostly odoriferous esters: — *ethyl α-acetoxy*iso*hexoate,* b. p. 120 to 121°/20 mm., the corresponding *methyl* ester, b. p. 99 to 100°/20 mm.; *ethyl α-benzoyl*iso*hexoate,* b. p. 174 to 176°/17 mm.; *ethyl α-*iso*valeryl*iso*hexoate,* b. p. 125 to 128°/10 mm.; *ethyl* and *amyl α-chloro*iso*hexoates,* b. p. 152 to 153°/10 mm. and 113 to 114°/8 to 10 mm.²). These two esters can be converted into the corresponding esters of *iso*hexoic acid by reduction with sodium amalgam. α-Acetoxy*iso*hexoic acid phenyliminochloride forms prisms which when treated with acetic ester and magnesium yield α-ethoxy*iso*hexaldehyde as an oil.

Bergaptene. — As a continuation of their earlier endeavour³) to obtain bergaptene and xanthotoxin synthetically, P. Karrer, A. Rüdlinger, A. Glattfelder, and L. Waitz⁴) were successful in confirming the constitution suggested for the 2-methyl-5-hydroxycoumarone-4-acrylic acid described formerly. It remained, therefore, still unanswered why the coumarone ring prevents the closing of the coumarin ring. The authors now regard the formula suggested by Thoms³) for bergaptene as uncertain. With the purpose of elucidating this question the authors undertook to arrive at bergaptene from phloroglucinol monomethyl ether *via* methoxy-7-acetoxycoumarin. Unfortunately it was impossible to add bromine to the double bond of the coumarin ring without simultaneous bromination of the nucleus, so that the experiment had to be broken off.

Glucosides.

R. H. Clark and K. B. Gillie⁵) determined the *salicin* content in the bark of various British Columbian willows and poplars. The bark was dried for 48 hours at a temperature of about 110° and digested for three hours with boiling water. The proteins were removed by adding lead acetate and the filtrate treated with emulsin. When hydrolysis had passed off the amount of the glucose formed was estimated with Fehling's solution. The salicin content of the various barks proved to vary considerably; in the most cases the spring barks gave higher values than the corresponding autumn barks.

Species	Average salicin content samples autumn	spring
*Salix Nuttallii*⁶)	3.90 per cent.	4.49 per cent.
Salix Hookeriana	9.81 „ „	5.09 „ „
Salix sitchensis	2.80 „ „	7.38 „ „
Salix lasiandra	2.50 „ „	2.51 „ „
Salix purpurea	—	3.83 „ „
Populus trichocarpa	0.955 „ „	3.86 „ „
Populus tremuloides	3.77 „ „	2.45 „ „

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¹) *Journ. Tokyo chem. Soc.* **41** (1920), 965. As per *Journ. chem. Soc.* **120** (1921), I. 220. — ²) Evidently, there is here some mistake concerning the boiling points. — ³) Cf. *Bericht* (Germ. ed.) **1921**, 123. — ⁴) *Helv. chim. acta* **4** (1921), 718. — ⁵) *Americ. Journ. Pharm.* **93** (1921), 618. — ⁶) This species is not recorded in the *Index Kewensis* of **1910**.

Nitrogenous Bodies.

According to L. Rosenthaler[1], the youngest leaves of the cherry laurel, as long as they are not fully developed, show the highest content of *hydrocyanic acid.* Later on, the differences in growth are no more marked to such an extent. Both halves of the leaf, likewise the outer and the inner part, or the upper and the lower part, contain very nearly the same quantity of the acid. The central nerve, however, especially in young leaves, is richer in hydrocyanic acid than the leaf tissue.

Sulphocyanic acid was proved to be present by S. Dezani[2] in the extracts of the roots of *Brassica Rapa,* L., *Cochlearia Armoracia,* L., and *Raphanus sativus,* L., in the fresh herb of *Raphanus Raphanistrum,* Cav. Desc., *Thlaspi bursa pastoris,* L., *Calepina Corvini,* Desv., *Sisymbrium Alliaria,* Scop., *S. officinale,* Scop., *Nasturtium officinale,* R. Br., *Bunias Erucago,* L., *Eruca sativa,* Mill., *Sinapis alba,* L., *S. nigra,* L., and *S. arvensis,* L. The sulphocyanic acid occurs probably as such in the plants and is not a decomposition-product of a mustard oil.

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[1] *Schweiz. Apoth.-Ztg.* **59** (1921), 10 and 22. As per *Chem. Zentralbl.* **1921,** I, 774. — [1] *Staz. sperim. agrar. ital.* **53** (1920), 438. As per *Chem. Zentralbl.* **1921,** I. 814.

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